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Publication number:

0 364 844 B1

12

EUROPEAN PATENT SPECIFICATION

- (45) Date of publication of patent specification: **16.03.94** (51) Int. Cl.⁵: **C07D 213/61, A01N 47/44, C07D 213/75, C07D 239/26, C07D 277/32, A01N 47/42**
- (21) Application number: **89118689.2**
- (22) Date of filing: **07.10.89**

The file contains technical information submitted after the application was filed and not included in this specification

(54) **Insecticidally active cyano compounds.**

(30) Priority: **21.10.88 JP 264020/88**
13.03.89 JP 57813/89

(43) Date of publication of application:
25.04.90 Bulletin 90/17

(45) Publication of the grant of the patent:
16.03.94 Bulletin 94/11

(84) Designated Contracting States:
BE CH DE FR GB IT LI NL

(56) References cited:
EP-A- 0 235 725
FR-A- 2 294 703
FR-A- 2 611 114

CHEMICAL ABSTRACTS, vol. 90, 1979 page 608, abstract no. 87289f, Columbus, Ohio, US; & **JP-A-78 108 970**

JOURNAL OF MEDICINAL CHEMISTRY, vol. 21, no. 8, August 1978, pages 773-781, American Chemical Society; H.J. PETERSEN: "Synthesis and hypotensive activity of N-alkyl-N''-cyano-N'-pyridylguanidines"

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EP 0 364 844 B1

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Description

The present invention relates to novel cyano compounds, to processes for their preparation and to their use as insecticides.

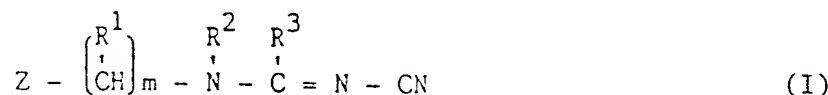
It has already been disclosed that certain N-cyanoisothioureas are useful as medicaments for treating ulcers (see Japanese Patent Laid-open No. 234,064/1987), and that the N-cyanoisothioureas disclosed in the above Japanese patent application and other N-cyanoisothioureas have also a function for controlling insects and plant-destructive nematodes (see Japanese Patent Laid-open No. 233,903/1988 and EP-OS 303,570), and furthermore that certain N-cyanoguanidines have insecticidal function (see Japanese Patent Laid-open No. 47,766/1989).

Substituted Cyanoguanidines are furthermore known from FR-A 2 294 703, J.med.Chem. Vol 21 (1978) p. 773-781, Chemical Abstracts, Vol. 90; abstract No. 87 289f but no insecticidal properties have been disclosed for these compounds.

2-Cyanoimino-imidazolines having insecticidal properties are known from EP-OS 235 725 but are not always satisfying.

Subject of the present invention is:

1) Use of cyano compounds of the formula (I)



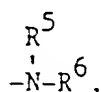
wherein R¹ is hydrogen, cyano or C₁₋₄ alkyl,

m is 0 or 1,

R² is hydrogen, C₁₋₆ alkyl, C₃₋₄ alkenyl optionally substituted by halogen,

C₃₋₄ alkynyl, C₃₋₈ cycloalkyl optionally substituted by methyl, optionally halogen substituted phenyl, optionally halogen substituted benzyl, hydroxy, C₁₋₄ alkoxy or -CH₂-Z, in which Z has the same meanings as stated below,

R³ is -O-R⁴, -S-R⁴ or



in which R⁴ is C₁₋₆ alkyl, C₃₋₄ alkenyl,

C₃₋₄ alkynyl, C₃₋₈ cycloalkyl, optionally halogen substituted phenyl, optionally halogen substituted benzyl or -(CH₂)_n-Z, in which n is 1 or 2 and

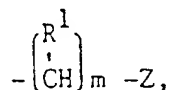
Z has the same meanings as stated below, and

R⁵ and R⁶ are hydrogen, C₁₋₉ alkyl optionally substituted by at least one selected from a group consisting of halogen, hydroxy, mercapto, C₁₋₂ alkoxy, C₁₋₂ alkylthio,

C₃₋₆ cycloalkyl, amino, C₁₋₂ monoalkylamino,

C₂₋₄ (in total) di-alkylamino, carboxy, C₁₋₂ alkoxy-carbonyl and cyano, C₃₋₄ alkenyl optionally substituted by halogen,

C₃₋₄ alkynyl, optionally chlorine substituted phenyl, optionally chlorine substituted benzyl C₁₋₄ alkoxy, hydroxy, formyl, C₁₋₄ alkoxy-carbonyl, C₁₋₄ alkylamino, C₂₋₄ (in total) di-alkylamino, amino, acyl or



in which R¹ and m have the same meanings as stated above, and Z has the same meanings as stated below, and in addition,

R⁵ and R⁶ may form, together with the N-atom to which they are bonded, a 3 to 7 membered ring which may be substituted by C₁₋₂ alkyl and may contain N, O or S as the member of said ring, besides the N-

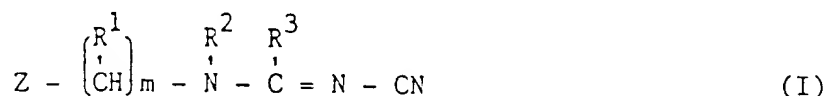
atom to which they are bonded, and

Z is a 5 membered heterocyclic group which is substituted by halogen or C₁₋₂ alkyl and contains one or two nitrogen atoms, or one nitrogen atom and either one oxygen atom or one sulfur atom, or

a 6 membered heterocyclic group which is substituted by halogen or

C₁₋₂ alkyl and contains one or two nitrogen atoms, provided that where Z is pyridyl substituted by halogen, m is 1, R² is C₁₋₆ alkyl and R³ is -S-alkyl(C₁₋₆) or -S-benzyl, then R¹ is cyano or C₁₋₄ alkyl for combating harmful insects.

Novel cyano compounds of the formula (I)



wherein R¹ is hydrogen, cyano or C₁₋₄ alkyl,

m is 1,

R² is hydrogen, C₁₋₆ alkyl, C₃₋₄ alkenyl optionally substituted by halogen,

C₃₋₄ alkynyl, C₃₋₈ cycloalkyl optionally substituted by methyl, optionally halogen-substituted phenyl,

optionally halogen-substituted benzyl, hydroxy, C₁₋₄ alkoxy or -CH₂-Z, in which Z has the same meanings as stated below,

R³ is -O-R⁴, -S-R⁴ or



in which R⁴ is C₁₋₆ alkyl, C₃₋₄ alkenyl,

C₃₋₄ alkynyl, C₃₋₈ cycloalkyl, optionally halogen-substituted phenyl, optionally halogen-substituted benzyl or -(CH₂)_n-Z, in which n is 1 or 2 and

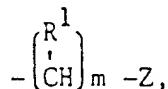
Z has the same meanings as stated below, and

R⁵ and R⁶ are hydrogen, C₁₋₉ alkyl optionally substituted by at least one selected from a group consisting of halogen, hydroxy, mercapto, C₁₋₂ alkoxy, C₁₋₂ alkylthio,

C₃₋₆ cycloalkyl, amino, C₁₋₂ monoalkylamino,

C₂₋₄ (in total) di-alkylamino, carboxy, C₁₋₂ alkoxy-carbonyl and cyano, C₃₋₄ alkenyl optionally substituted by halogen,

C₃₋₄ alkynyl, optionally chlorine-substituted phenyl, optionally chlorine-substituted benzyl, C₁₋₄ alkoxy, hydroxy, formyl, C₁₋₄ alkoxy-carbonyl, C₁₋₄ alkylamino, C₂₋₄ (in total) di-alkylamino, amino, acyl or



in which R¹ and m have the same meanings as stated above, and Z has the same meanings as stated below, and in addition,

R⁵ and R⁶ may form, together with the N-atom to which they are bonded, a 3 to 7 membered ring which may be substituted by C₁₋₂ alkyl and may contain N, O or S as the member of said ring, besides the N-atom to which they are bonded, and

Z is a 5 membered heterocyclic group which is substituted by halogen or C₁₋₂ alkyl and contains one or two nitrogen atoms, or one nitrogen atom and either one oxygen atom or one sulfur atom, or

a 6 membered heterocyclic group which is substituted by halogen or C₁₋₂ alkyl and contains one or two nitrogen atoms,

provided that where Z is pyridyl substituted by halogen, m is 1, R² is C₁₋₆ alkyl and R³ is S-alkyl(C₁₋₆) or -S-benzyl, then R¹ is cyano or C₁₋₄ alkyl and furthermore with the exception of N-cyano-N'-methyl-N''-[(4-methyl-thiazol-2-yl)methyl]guanidine.

The novel compounds of the formula (I) can be obtained when

a) in the case where R^3 is $-S-R^4$;
compounds of the formula (II)



wherein R^1 , m , R^2 and Z have the same meanings as stated above, are reacted with compounds of the formula (III)



wherein R^4 has the same meaning as stated above, in the presence of inert solvents,

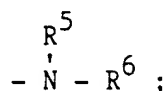
b) in the case where R^3 is $-O-R^4$;

the aforesaid compounds of the formula (II) are reacted with compounds of the formula (IV)



wherein R^4 has the same meaning as stated above, in the presence of inert solvents,

c) in the case where R^3 is



the aforesaid compounds of the formula (II) are reacted with compounds of the formula (V)



wherein R^4 , R^5 , and R^6 have the same meanings as stated above, in the presence of inert solvents,

d) in the case where R^3 is $-S-R^4$ and m is 1; compounds of the formula (VI)



wherein R^1 and Z have the same meanings as stated above, and M is halogen,
are reacted with compounds of the formula (VII)



wherein R^2 and R^4 have the same meanings as stated above,
in the presence of inert solvents and if appropriate in the presence of a base.

The novel cyano compounds exhibit powerful insecticidal properties.

Surprisingly, the cyano compounds, according to the invention exhibit a substantially greater insecticidal function than those known from the aforementioned prior arts.

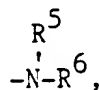
Among the cyano compounds according to the invention, of the formula (I), preferred compounds are those in which

R^1 is hydrogen or C_{1-3} alkyl,

m is 0 or 1,

R^2 is hydrogen, C_{1-4} alkyl, allyl, propargyl, phenyl optionally substituted by halogen, benzyl optionally substituted by halogen, hydroxy, C_{1-3} alkoxy or $-CH_2-Z^1$ in which Z^1 is pyridyl optionally substituted by halogen,

R^3 is $-O-R^4$, $-S-R^4$ or



in which

R^4 is C_{1-4} alkyl, allyl, propargyl, C_{3-6} cycloalkyl, phenyl optionally substituted by halogen, benzyl optionally substituted by halogen or $-CH_2-Z^1$ in which

Z^1 has the same meaning as stated above,

R^5 and R^6 are hydrogen, C_{1-9} alkyl optionally substituted by fluorine or chlorine, allyl optionally substituted by chlorine, propargyl, phenyl optionally substituted by chlorine, benzyl optionally substituted by chlorine, C_{1-3} alkoxy, hydroxy, hydroxy- C_{1-2} alkyl, mercapto- C_{1-2} alkyl, amino- C_{1-2} alkyl, C_{1-3} alkylamino, dimethylamino, amino, cyano- C_{1-2} alkyl, pyridyl optionally substituted by chlorine or methyl, or $-CH_2-Z^2$ in which Z^2 is pyridyl optionally substituted by halogen or 5-thiazolyl optionally substituted by halogen,

and in addition,

R^5 and R^6 may form, together with the N-atom to which they are bonded, a 3 to 6 membered ring which may be substituted by methyl and may contain N, O or S as the member of said ring, besides the N-atom to which they are bonded, and

Z is a 5 membered heterocyclic group which is substituted by halogen or C_{1-2} alkyl and contains one or two nitrogen atoms, or one nitrogen atom and either one oxygen atom or one sulfur atom, or

a 6 membered heterocyclic group which is substituted by halogen or C_{1-2} alkyl and contains one or two nitrogen atoms, provided that where Z is pyridyl substituted by halogen, m is 1, R^2 is C_{1-4} alkyl and

R^3 is $-S-alkyl(C_{1-4})$ or $-S-benzyl$, then R^1 is C_{1-3} alkyl.

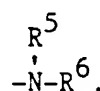
Very particularly preferred cyano compounds of the formula (I) are those in which

R^1 is hydrogen, methyl, ethyl or propyl,

m is 0 or 1

R^2 is hydrogen, methyl, ethyl, propyl, allyl, propargyl, phenyl optionally substituted by chlorine, hydroxy, methoxy, ethoxy or pyridylmethyl optionally substituted by chlorine,

R^3 is $-O-R^4$, $-S-R^4$ or



in which

R^4 is C_{1-3} alkyl, allyl, propargyl, cyclohexyl, phenyl, benzyl optionally substituted by chlorine, pyridyl-methyl optionally substituted by chlorine,

R⁵ and R⁶ are hydrogen, C₁₋₄ alkyl optionally substituted by fluorine or chlorine, allyl optionally substituted by chlorine, propargyl,

phenyl optionally substituted by chlorine, benzyl optionally substituted by chlorine, methoxy, hydroxy, hydroxyethyl, C₁₋₂ alkylamino, dimethylamino, amino, cyanoethyl,

5 2-chloro-5-pyridylmethyl or 2-chloro-5-thiazolylmethyl, and in addition,

R⁵ and R⁶ may form, together with the N-atom to which they are bonded, pyrrolidino, piperidino, 2-methylpiperidino, morpholino, piperazino or isoxazolidino, and Z is a 5 membered heterocyclic group which is substituted by halogen or C₁₋₂ alkyl and contains one or two nitrogen atoms, or one nitrogen atom and either one oxygen atom or one sulfur atom, or a 6 membered heterocyclic group which is substituted by halogen or C₁₋₂ alkyl and contains one or two nitrogen atoms, provided that where Z is pyridyl substituted by halogen, m is 1,

R² is methyl, ethyl or propyl and R³ is -S-alkyl(C₁₋₃) or -S-benzyl, then R¹ is methyl, ethyl or propyl.

Specifically, the following compounds may be mentioned:

S-methyl-N-(2-chloro-5-pyridylmethyl)-N'-cyanoisothiourea,

15 S-methyl-N-(2-chloro-5-thiazolylmethyl)-N'-cyanoisothiourea,

3-(2-chloro-5-pyridylmethyl)-3-methyl-2-cyanoguanidine,

3-(2-chloro-5-pyridylmethyl)-1-methyl-2-cyanoguanidine,

3-(2-chloro-5-pyridylmethyl)-1,1-dimethyl-2-cyanoguanidine,

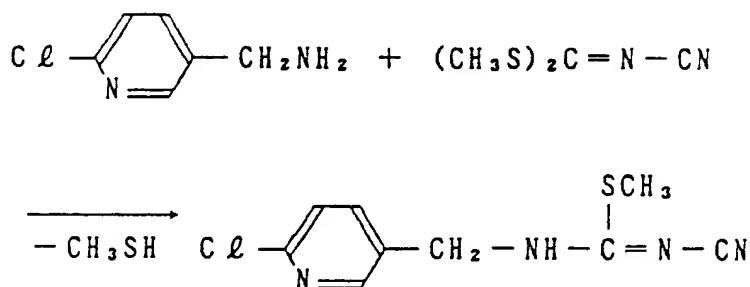
3-(2-chloro-5-pyridylmethyl)-1,3-dimethyl-2-cyanoguanidine,

20 3-(2-chloro-5-pyridylmethyl)-1,1,3-trimethyl-2-cyanoguanidine,

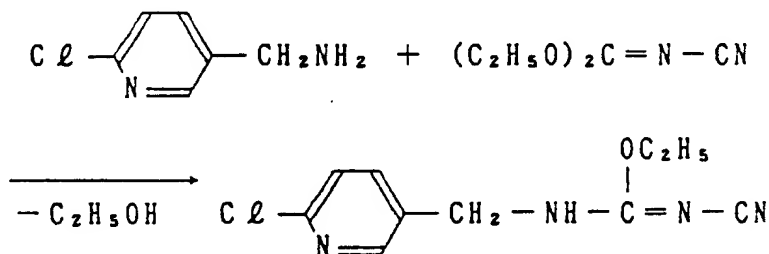
1,3-bis(2-chloro-5-pyridylmethyl)-2-cyanoguanidine, and

S-methyl-N-(2-chloro-5-thiazolylmethyl)-N'-cyanoisothiourea.

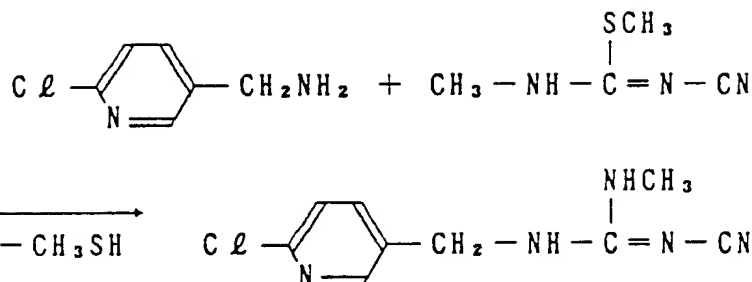
If, for example, in the process a), 5-aminomethyl-2-chloropyridine and dimethyl cyanamidodithiocarbonate are used as starting materials, the course of the reaction can be represented by the following equation:



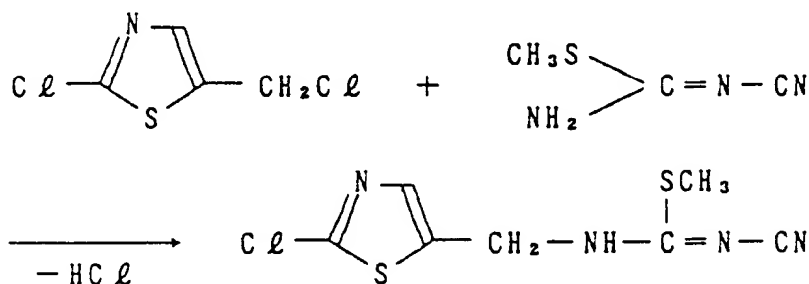
If, for example, in the process b), 5-aminomethyl-2-chloropyridine and diethyl cyanamidocarbonate are used as starting materials, the course of the reaction can be represented by the following equation:



If, for example, in the process c), 5-aminomethyl-2-chloropyridine and 3-cyano-1-methyl-2-methylisothiourea are used as starting materials, the course of the reaction can be represented by the following equation:



If, for example, in the process d), 2-chloro-5-chloromethylthiazole and 3-cyano-2-methylisothiurea are used as starting materials, the course of the reaction can be represented by the following equation:



In the process a), the compounds of the formula (II) as a starting material mean ones based on the aforementioned definitions of R^1 , m , R^2 and Z .

In the formula (II), R^1 , m , R^2 and Z has preferably the same meanings as already given above.

The compounds of the formula (II) include known compounds which have been described in USP 4,499,907 and Nihon Kagaku Zasshi (Periodical of Japanese Chemistry), vol. 83, pp. 218 - 222, 1962, and as examples thereof, there may be mentioned:

5-aminomethyl-2-chloropyridine,
5-aminomethyl-2-chlorothiazole and
5-methylaminomethyl-2-chloropyridine.

The compounds of the formula (III), as also a starting material in the process a), mean ones based on the aforementioned definition of R^4 .

In the formula (III), R^4 has preferably the same meaning as already given above.

The compounds of the formula (III) are known compounds described in for instance Japanese Patent Publication No. 26,482/1969, and as examples, cyanamidodithio dimethylcarbonate may be exemplified.

In the process b), the compounds of the formula (IV) as a starting material mean ones based on the aforementioned definition of R^4 .

In the process b), R^4 has preferably the same meaning as already given above.

The compounds of the formula (IV) are known compounds described in Japanese Patent Laid-open No. 126,856/1988, and as examples, cyanamido diethylcarbonate may be exemplified.

In the process c), the compounds of the formula (V) as a starting material mean ones based on the aforementioned definitions of R^4 , R^5 and R^6 .

In the formula (V), R^4 , R^5 and R^6 have preferably the same meanings as already given above.

The compounds of the formula (V) may be obtained in general when the aforementioned compounds of the formula (III) are reacted with compounds of the formula (VIII)



wherein R^5 and R^6 have the same meanings as stated above,
in the presence of inert solvents.

The above compounds of the formula (VIII) are well-known in organic chemistry.

In the process d), the compounds of the formula (VI) as a starting material mean ones based on the
aforementioned definitions of R^1 , Z and M.

In the formula (VI), R^1 and Z have preferably the same meanings as already given above, and M preferably represents chlorine or bromine.

The compounds of the formula (VI) are known compounds described in Japanese Patent Laid-open No. 81,382/1987, and as examples, there may be mentioned:

2-chloro-5-chloromethylthiazole and
2-chloro-5-chloromethylpyridine.

The compounds of the formula (VII), as also a starting material in the process d), mean ones based on the aforementioned definitions of R^2 and R^4 .

In the formula (VII), R^2 and R^4 have preferably the same meanings as already given above.

The compounds of the formula (VII), in the same way as the above process for the preparation of the compounds of the formula (V), may be obtained when the aforementioned compounds of the formula (III) are reacted with compounds of the formula (IX)

$R^2 - NH_2$ (IX)

wherein R^2 has the same meaning as stated above,
in the presence of inert solvents,

The above compounds of the formula (IX) are well-known.

Suitable diluents in the process a) are all inert organic solvents.

As examples, these preferentially include water;
aliphatic, cycloaliphatic and aromatic, optionally chlorinated, hydrocarbons, such as hexane, cyclohexane, petroleum ether, ligroin, benzene, toluene, xylene, methylene chloride, chloroform, carbon tetrachloride, ethylene chloride, trichloroethylene, chlorobenzene and the like; ethers such as diethyl ether, methyl ethyl ether, di-isopropyl ether, dibutyl ether, propylene oxide, dioxane, tetrahydrofuran and the like; ketones such as acetone, methylethyl ketone, methyl-iso-propyl ketone, methyl-iso-butyl ketone; nitriles such as acetonitrile, propionitrile, acrylonitrile and the like; alcohols such as methanol, ethanol, iso-propanol, butanol, ethylene glycol and the like; esters such as ethyl acetate, amyl acetate; acid amides such as dimethyl formamide, dimethyl acetamide and the like; and sulfones and sulfoxides such as dimethyl sulfoxide, sulfolane and the like; and bases, for example, such as pyridine.

The reaction temperature of the process a) can be varied within a substantial range.
In general, the reaction is carried out at between about 0 and about 150 °C, preferably between about 20 °C and about 100 °C.

The reaction of the process a) can be carried out under normal, elevated or reduced pressure.

In carrying out the process a), for example, about 1 to 1.2 moles, preferably 1.1 moles of the compounds of the formula (III) may be employed per mole of the compounds of the formula (II), and these compounds are each other reacted in the presence of inert solvents, for example, alcohol until the generation of mercaptan has ceased so that the aimed compounds of the formula (I) can be obtained.

In carrying the process b), suitable diluents include the same solvents as exemplified for the process a).

The reaction temperatures of the process b) can be varied within a substantial range. In general, the reaction is carried out at between about 0 and about 150 °C, preferably between 20 °C and about 80 °C.

The reaction of the process b) can be carried out under normal, elevated or reduced pressure.

In carrying out the process b), for example, about 1 to 1.2 moles, preferably about 1 to 1.1 moles of the compounds of the formula (IV) may be employed per mole of the compounds of the formula (II), and these compounds are each other reacted in the presence of inert solvents, for example alcohol, so that the aimed compounds of the formula (I) can be obtained.

In carrying the process c), suitable diluents include the same solvents as exemplified for the process a).

The reaction temperatures of the process c) can be varied within a substantial range. In general, the reaction is carried out at between about 0 and about 150 °C, preferably between 20 °C and about 100 °C.

The reaction of the process c) can be carried out under normal, elevated or reduced pressure.

In carrying out the process c), for example, about 1 to 1.2 moles, preferably about 1 to 1.1 moles of the compounds of the formula (V) may be employed per mole of the compounds of the formula (II), and these compounds are mixed up heating, so that the aimed compounds of the formula (I) can be obtained.

In carrying the process d), suitable diluents include the same solvents as exemplified for the process a), in addition also ketones such as acetone, methylethyl ketone, methylisopropyl ketone, methyl iso-butyl ketone.

The process d) can be carried out in the presence of a base.

As examples of bases, these preferentially include, for example, potassium hydroxide, sodium hydroxide, sodium hydride, sodium carbonate, potassium carbonate, sodium methoxide, sodium ethoxide, potassium tert-butoxide, and tert-amines such as triethylamine, diethylaniline, pyridine and the like.

The reaction temperatures of the process d) can be varied within a substantial range. In general, the reaction is carried out at between about 0 and boiling point of the reaction mixture preferably between about 0 and about 80 ° C.

The reaction of the process d) can be carried out under normal, elevated or reduced pressure.

In carrying out the process d), for example, about 0.8 to 1.2 moles, preferably about 0.9 to 1.1 moles of the compounds of the formula (VII) may be employed per mole of the compounds of the formula (VI), and these compounds are each other reacted in the presence of inert solvents, for example dimethylsulfoxide, so that the aimed compounds of the formula (I) can be obtained.

The active compounds are well tolerated by plants, have a favourable level of toxicity to warm-blooded animals, and can be used for combating arthropod pests, especially insects which are encountered in agriculture, in forestry, in the protection of stored products and of materials, and in the hygiene field. They are active against normally sensitive and resistant species and against all or some stages of development.

The above-mentioned pests include:

from the class of the Isopoda, for example Oniscus Asellus, Armadillidium vulgare and Porcellio scaber;

from the class of the Diplopoda, for example Blaniulus guttulatus;

from the class of the Chilopoda, for example Geophilus carpophagus and Scutigera spec.;

from the class of the Symphyla, for example Scutigera immaculata;

from the order of the Thysanura, for example Lepisma saccharina;

from the order of the Collembola, for example Onychiurus armatus;

from the order of the Orthoptera; for example Blatta orientalis, Periplaneta americana, Leucophaea maderae, Blattella germanica, Acheta domesticus, Gryllotalpa spp., Locusta migratoria migratorioides, Melanoplus differentialis and Schistocerca gregaria;

from the order of the Dermaptera, for example Forficula auricularia;

from the order of the Isoptera, for example Reticulitermes spp.;

from the order of the Anoplura, for example Phylloxera vastatrix, Pemphigus spp., Pediculus humanus corporis, Haematopinus spp. and Linognathus spp.;

from the order of the Mallophaga, for example Trichodectes spp. and Damalinea spp.;

from the order of the Thysanoptera, for example Hercinothrips femoralis and Thrips tabaci,

from the order of the Heteroptera, for example Eurygaster spp., Dysdercus intermedius, Piesma quadrata, Cimex lectularius, Rhodnius prolixus and Triatoma spp.;

from the order of the Homoptera, for example Aleurodes brassicae, Bemisia tabaci, Trialeurodes vaporariorum, Aphis gossypii, Brevicoryne brassicae, Cryptomyzus ribis, Aphis fabae, Doralis pomi, Eriosoma lanigerum, Hyalopteris arundinis, Macrosiphum avenae, Myzus spp., Phorodon humuli, Rhopalosiphum padi, Empoasca spp., Euscelis bilobatus, Nephotettix cincticeps, Lecanium corni, Saissetia oleae, Laodelphax striatellus, Nilaparvata lugens, Aonidiella aurantii, Aspidiotus hederae, Pseudococcus spp. and Psylla spp.;

from the order of the Lepidoptera, for example Pectinophora gossypiella, Bupalus piniarius, Cheimatobia brumata, Lithocolletis blancardella, Hyponomeuta padella, Plutella maculipennis, Malacosoma neustria, Euproctis chrysorrhoea, Lymantria spp., Bucculatrix thurberiella, Phyllocnistis citrella, Agrotis spp., Euxoa spp., Feltia spp., Earias insulana, Heliothis spp., Spodoptera exigua, Mamestra brassicae, Panolis flammea, Prodenia litura, Spodoptera spp., Trichoplusia ni, Carpocapsa pomonella, Pieris spp., Chilo spp., Pyrausta nubilalis, Ephestia kuehniella, Galleria mellonella, Cacoecia podana, Capua reticulana, Choristoneura fumiferana, Clysia ambiguella, Homona magnanima and Tortrix viridana;

from the order of the Coleoptera, for example Anobium punctatum, Rhizopertha dominica, Acanthoscelides obtectus, Acanthoscelides obtectus, Hylotrupes bajulus, Agelastica alni, Leptinotarsa decemlineata, Phaedon cochleariae, Diabrotica spp., Psylliodes chrysocephala, Epilachna varivestis, Atomaria spp., Oryzaephilus surinamensis, Anthonomus spp., Sitophilus spp., Otiorrhynchus sulcatus, Cosmopolites sordidus, Ceuthorrhynchus assimilis, Hypera postica, Dermestes spp., Trogoderma spp., Anthrenus spp., Attagenus spp., Lyctus spp., Meligethes aeneus, Ptinus spp., Niptus hololeucus, Gibbium psyllioides, Tribolium spp., Tenebrio molitor, Agriotes spp., Conoderus spp., Melolontha melolontha, Amphimallon solstitialis and Costelytra zealandica;

from the order of the Hymenoptera for example Diprion spp., Hoplocampa spp., Lasius spp., Monomorium pharaonis and Vespa spp.;

from the order of the Diptera, for example Aedes spp., Anopheles spp., Culex spp., Drosophila melanogaster, Musca spp., Fannia spp., Calliphora erythrocephala, Lucilia spp., Chrysomya spp., Cuterebra spp., Gastrophilus spp., Hyppobosca spp., Stomoxys spp., Oestrus spp., Hypoderma spp., Tabanus spp., Tannia spp., Bibio hortulanus, Oscinella frit, Phorbia spp., Pegomya hyoscyami, Ceratitis capitata, Dacus oleae and Tipula paludosa;

from the order of the Siphonaptera, for example Xenopsylla cheopis and Ceratophyllus spp.;

from the class of the Arachnida, for example Scorpio maurus and Latrodectus mactans;

from the order of the Arana, for example Acarus siro, Argas spp., Ornithodoros spp., Dermanyssus gallinae, Eriophyes ribis, Phyllocoptura oleivora, Boophilus spp., Rhipicephalus spp., Amblyomma spp., Hyalomma spp., Ixodes spp., Psoroptes spp., Chorioptes spp., Sarcoptes spp., Tarsonemus spp., Bryobia praetiosa, Panonychus spp. and Tetranychus spp..

The plant-parasitic nematodes include Pratylenchus spp., Radopholus similis, Ditylenchus dipsaci, Tylenchulus semipenetrans, Heterodera spp., Meloidogyne spp., Aphelenchoides spp., Longidorus spp., Xiphinema spp., and Trichodorus spp..

Furthermore, in the field of veterinary medicine, the novel compound of the present invention can effectively be employed for combating a variety of noxious animal-parasitic pests (internal- and external-parasitic pests), e.g. parasitic insects and nematodes. Such animal-parasitic pests may be exemplified as follows:

From the class of Insecta, e.g. Gastrophilus spp., Stomoxys spp., Tricodectes spp., Rhodnius spp., Ctenocephalides canis and the like.

The active compounds can be converted into the customary formulations, such as solutions, emulsions, wettable powders, suspensions, powders, foams, pastes, granules, aerosols, natural and synthetic materials impregnated with active compound, very fine capsules in polymeric substances, coating compositions for use on seed, and formulations used with burning equipment, such as fumigating cartridges, fumigating cans and fumigating coils, as well as ULV cold mist and warm mist formulations.

These formulations may be produced in known manner, for example by mixing the active compounds with extenders, that is to say liquid or liquefied gaseous or solid diluents or carriers, optionally with the use of surface-active agents, that is to say emulsifying agents and/or dispersing agents and/or foam-forming agents. In the case of the use of water as an extender, organic solvents can, for example, also be used as auxiliary solvents.

As liquid solvents diluents or carriers, there are suitable in the main, aromatic hydrocarbons, such as xylene, toluene or alkyl naphthalenes, chlorinated aromatic or chlorinated aliphatic hydrocarbons, such as chlorobenzenes, chloroethylenes or methylene chloride, aliphatic hydrocarbons, such as cyclohexane or paraffins, for example mineral oil fractions, alcohols, such as butanol or glycol as well as their ethers and esters, ketones, such as acetone, methyl ethyl ketone, methyl isobutyl ketone or cyclohexanone, or strongly polar solvents, such as dimethylformamide and dimethyl-sulphoxide, as well as water.

By liquefied gaseous diluents or carriers are meant liquids which would be gaseous at normal temperature and under normal pressure, for example aerosol propellants, such as halogenated hydrocarbons as well as butane, propane, nitrogen and carbon dioxide.

As solid carriers there may be used ground natural minerals, such as kaolins, clays, talc, chalk, quartz, attapulgite, montmorillonite or diatomaceous earth, and ground synthetic minerals, such as highly-dispersed silicic acid, alumina and silicates. As solid carriers for granules there may be used crushed and fractionated natural rocks such as calcite, marble, pumice, sepiolite and dolomite, as well as synthetic granules of inorganic and organic meals, and granules of organic material such as sawdust, coconut shells, maize cobs and tobacco stalks.

As emulsifying and/or foam-forming agents there may be used non-ionic and anionic emulsifiers, such as polyoxyethylene-fatty acid esters, polyoxyethylene-fatty alcohol ethers, for example alkylaryl polyglycol ethers, alkyl sulphonates, alkyl sulphates, aryl sulphonates as well as albumin hydrolysis products. Dispersing agents include, for example, lignin sulphite waste liquors and methylcellulose.

Adhesives such as carboxymethylcellulose and natural and synthetic polymers in the form of powders, granules or latices, such as gum arabic, polyvinyl alcohol and polyvinyl acetate, can be used in the formulation.

It is possible to use colorants such as inorganic pigments, for example iron oxide, titanium oxide and Prussian Blue, and organic dyestuffs, such as alizarin dyestuffs, azo dyestuffs or metal phthalocyanine dyestuffs, and trace nutrients, such as salts of iron, manganese boron, copper, cobalt, molybdenum and zinc.

The formulations in general contain from 0.1 to 95 per cent by weight of active compound, preferably from 0.5 to 90 per cent by weight.

The active compounds according to the invention can be present in their commercially available formulations and in the use forms, prepared from these formulations, as a mixture with other active compounds, such as insecticides, baits, sterilising agents, acaricides, nematocides, fungicides, growth-regulating substances or herbicides. The insecticides include, for example, phosphates, carbamates, carboxylates, chlorinated hydrocarbons, phenylureas, substances produced by microorganisms.

The active compounds according to the invention can furthermore be present in their commercially available formulations and in the use forms, prepared from these formulations, as a mixture with synergistic agents. Synergistic agent are compounds which increase the action of the active compounds, without it being necessary for the synergistic agent added to be active itself.

The active compound content of the use forms prepared from the commercially available formulations can vary within wide limits. The active compound concentration of the use forms can be from 0.0000001 to 100% by weight of active compound, preferably between 0.0001 and 1% by weight.

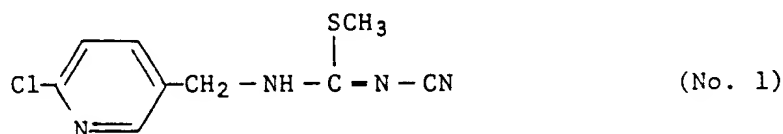
The compounds are employed in a customary manner appropriate for the use forms.

When used against hygiene pests and pests of stored products, the active compounds are distinguished by an excellent residual action on wood and clay as well as a good stability to alkali on limed substrates.

The preparation and use of the active compounds according to the invention can be seen from the following examples.

Examples of Preparation:

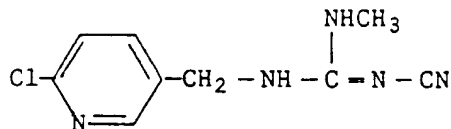
Example 1:



5-aminomethyl-2-chlorpyridine (1.43 g) and cyanamidedithio dimethyl carbonate (1.46 g) were dissolved in methanol (20 ml), while the solution was refluxed under heating for six hours.

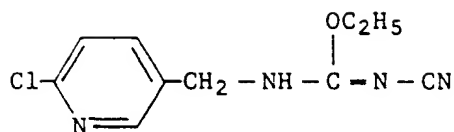
After being allowed to cool, the separated crystals were filtered to obtain the aimed S-methyl-N-(2-chloro-5-pyridylmethyl)-N'-cyanoisothiourea (1.2 g) having a melting point of from 191 to 194 °C.

Example 2:



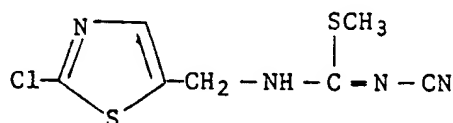
A mixture of 3-cyano-1-methyl-2-methylisothiourea (0.65 g) and 5-aminomethyl-2-chloropyridine (0.72 g) was stirred under heating at 100 °C for three hours. Then, the reaction product was cooled to room temperature and then purified on silica gel column chromatography (eluent: ethanol/chloroform) to obtain the aimed 3-(2-chloro-5-pyridylmethyl)-1-methyl-2-cyanoguanidine (0.5 g) having a melting point in the range of from 193 to 197 °C.

Example 3:



A mixture of 5-aminomethyl-2-chloropyridine (1.6 g), cyanamide dimethyl carbonate (1.6 g) and ethanol (30 ml) was refluxed under heating for four hours. Then, under reduced pressure, the ethanol contained in the reaction product was distilled off therefrom, followed by purification of the residue on silica gel chromatography (eluent: ethanol/chloroform) to obtain the aimed O-ethyl-N-(2-chloro-5-pyridylmethyl)-N'-cyanoisothiourea (1.7 g) having a melting point in the range of from 161 to 164 °C.

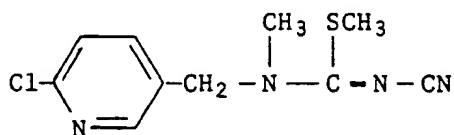
Example 4:



To a solution of 3-cyano-2-methylisothiourea (1.0 g) in dimethylformamide (30 ml) was portionwise added sodium hydride (0.22 g) at a temperature of from 0 to 5 °C, followed by stirring for one hour. Thereafter, 2-chloro-5-chloromethylthiazole (1.5 g) was added to the solution obtained above at a temperature of from 5 to 10 °C, followed by an overnight stirring at room temperature.

After the dimethylformamide contained in the solution had been distilled off under reduced pressure therefrom, the residue was washed with hexane, water, and chloroform in that order to obtain the aimed S-methyl-N-(2-chloro-5-thiazolylmethyl)-N'-cyano-isothiourea (0.4 g) having a melting point in the range of from 167 to 171 °C.

Example 5:

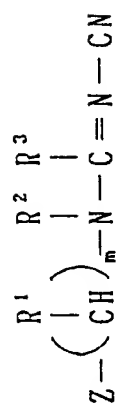


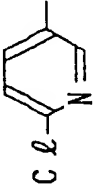
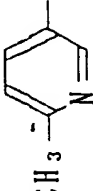
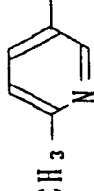
5-aminomethyl-2-chloropyridine (1.57 g) and cyanamidedithio dimethyl carbonate (1.46 g) were dissolved in methanol (10 ml), while the solution was refluxed under heating for ten hours.

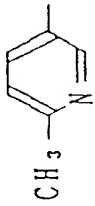
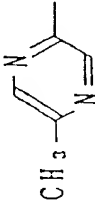
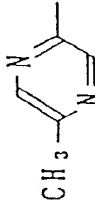
After being allowed to cool, the ethanol contained therein was distilled off from the solution and the thus obtained residue was purified on silica gel column chromatography (eluent: ethanol/chloroform) to obtain the aimed S,N-dimethyl-N-(2-chloro-5-chloropyridylmethyl)-N'-cyanoisothiourea (1.0 g) having n_D^{20} 1.6212.

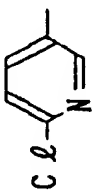
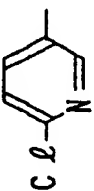
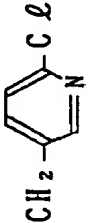
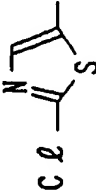
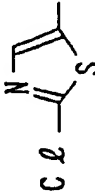
Together with the compounds prepared in Example 1 to Example 5, other compounds that can be obtained in the same way as said Examples are shown in the following Table 1:

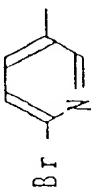
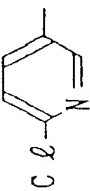
Table 1

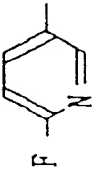
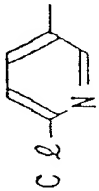
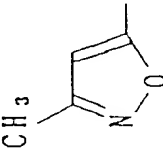


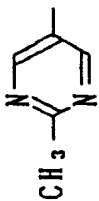
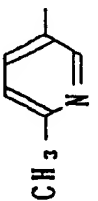

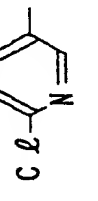
Comp. No.	Z	R ¹	m	R ²	R ³	Physical property
1		H	1	H	SCl ₃	mp. 191-194°C
2		H	1	H	SCl ₃	
3		H	1	CH ₃	SCl ₃	

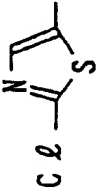
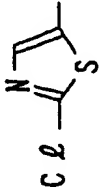
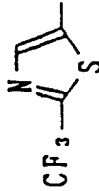
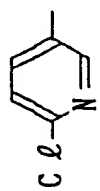
Comp. No.	Z	R ¹	m	R ²	R ³	Physical property
4		H	1	C ₂ H ₅	SCH ₃	mp. 163-166°C
5		H	1	H	SCH ₃	
6		CH ₃	1	H	SCH ₃	

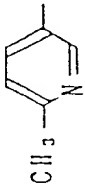
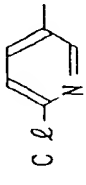
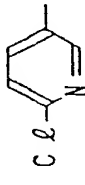
Comp No.	Z	R ¹	m	R ²	R ³	Physical property
8		CH ₃	1	H	SCH ₃	n_D^{20} 1.5895
9		H	1		SCH ₃	n_D^{20} 1.6285
10		H	1	H	SCH ₃	mp. 167-171°C
11		H	1	CH ₃	SCH ₃	

Comp. No.	Z	R ¹	m	R ²	R ³	Physical property
12		H	1	H	SCH ₃	
13		—	0	H	SCH ₃	mp. 139 - 142°C

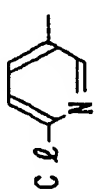
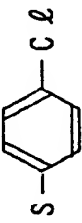
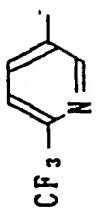
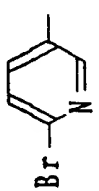
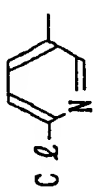
Comp No.	Z	R ¹	m	R ²	R ³	Physical property
17		CH ₃	1	C ₄ H ₉ -n	SCH ₃	n_D^{20} 1.6178
18		H	1	CH ₂ C≡CH	SCH ₃	
19		H		H	SCH ₃	

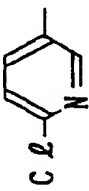
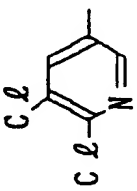
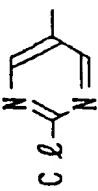
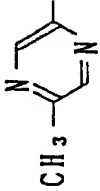
Comp. No.	Z	R ¹	m	R ²	R ³	Physical property
20		H		H	SCH ₃	mp. 152-153.5°C
21		H		H	SC ₂ H ₅	
22		H		H	SC ₂ H ₅	
23		H		CH ₃	SC ₂ H ₅	

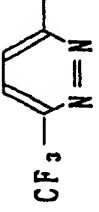
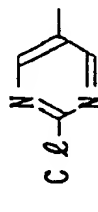
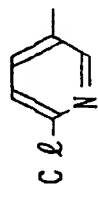
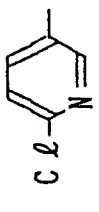
Comp No.	Z	R ¹	m	R ²	R ³	Physical property
24		H		H	SC ₂ H ₅	mp. 141.5- 143°C
25		—	0	H	SCH ₃	
26		C ₃ H ₇ -n	1	H	SC ₂ H ₅	
27		H	1	H	SC ₃ H ₇ -n	

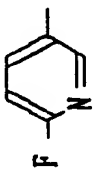
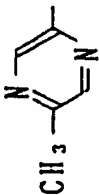

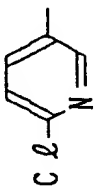
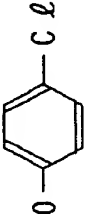
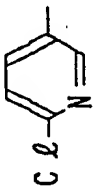
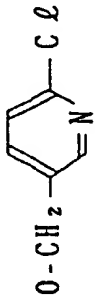
Comp No.	Z	R ¹	m	R ²	R ³	Physical property
28		H	1	CH ₃	SC ₃ H ₇ -n	
29		H	1	H	SC ₃ H ₇ -n	
30		H	1	H	SC ₄ H ₉ -n	

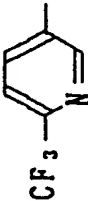
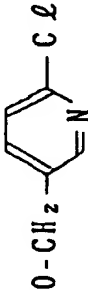
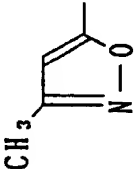
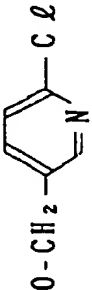
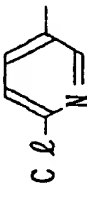
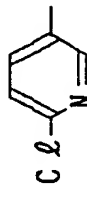
Comp No.	Z	R ¹	m	R ²	R ³	Physical property
32		H	1	H	$\text{SCH}_2\text{CH}=\text{CH}_2$	
33		H	1	H		
34		H	1	CH_3		
35		H	1	H		

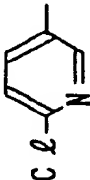
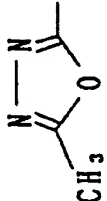
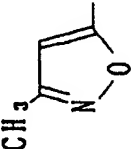
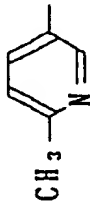
Comp. No.	Z	R ¹	m	R ²	R ³	Physical property
36		CH ₃	1	H		
37		C ₂ H ₅	1	H	OCH ₃	
38		H	1	C ₂ H ₅	OCH ₃	
39		H	1	H	OCH ₃	mp. 204-207°C

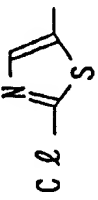
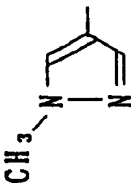
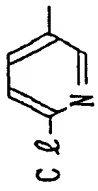
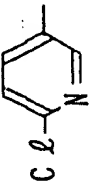
Comp No.	Z	R ¹	m	R ²	R ³	Physical property
40		H	1	CH ₃	OCH ₃	n_D^{20} 1.5755
41		H	1	CH ₃	OCH ₃	
42		H	1	H	OCH ₃	
43		H	1	C ₃ H ₇ -n	OCH ₃	

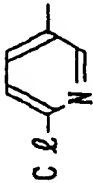
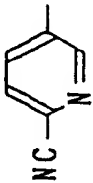
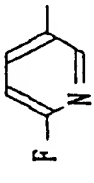
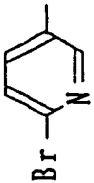
Comp No.	Z	R ¹	m	R ²	R ³	Physical property
44		H	1	H	OC ₂ H ₅	m.p. 161-164°C
45		H	1	H	OC ₂ H ₅	
46		H	1	H	OC ₂ H ₅	
47		H	1	CH ₃	OC ₂ H ₅	


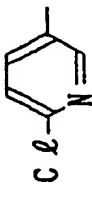
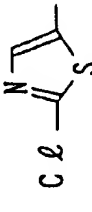
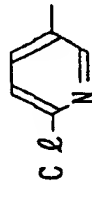
Comp No.	Z	R ¹	m	R ²	R ³	Physical property
48		H	1	H	OC ₃ H ₇ -n	
49		H	1	C ₂ H ₅		
50		H	1	H		
51		H	1	H		

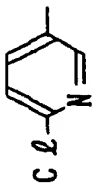
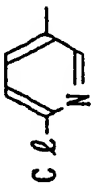
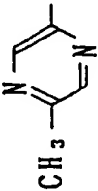
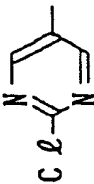
Comp No.	Z	R ¹	m	R ²	R ³	Physical property
52		H	1	CH ₃		m.p. 142-145°C
53		H	1	H		
54		H	1	H	NH ₂	m.p. 169-173°C
55		H	1	CH ₃	NH ₂	

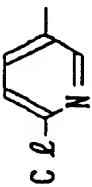
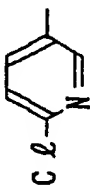
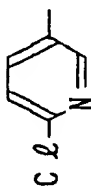
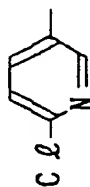
Comp No.	Z	R ¹	m	R ²	R ³	Physical property
56		—	0	H	NH ₂	
57		H	1	C ₃ H ₇ -n	NH ₂	
58		CH ₃	1	H	NH ₂	
59		C ₄ H ₉ -n	1	H	NH ₂	

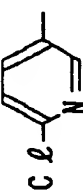
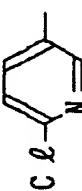
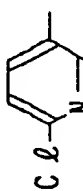
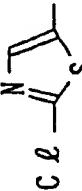
Comp No.	Z	R ¹	m	R ²	R ³	Physical property
60		H	1	CH ₃	NH ₂	
61		H	1	H	NHCH ₃	
62		H	1	H	NHCH ₃	mp. 193-197°C
63		H	1	CH ₃	NHCH ₃	mp. 113-118°C

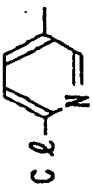
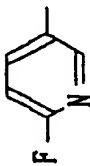
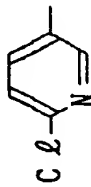
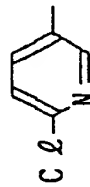
Comp No.	Z	R ¹	m	R ²	R ³	Physical property
64		—	0	H	NHCH ₃	
65		CH ₃	1	CH ₃	NHCH ₃	
66		H	1	H	NHCH ₃	
67		H	1	CH ₃	NHCH ₃	

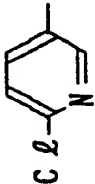
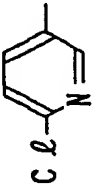
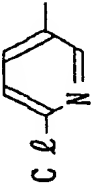
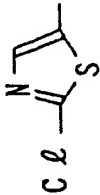
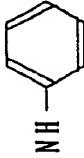
Comp No.	Z	R ¹	m	R ²	R ³	Physical property
68		H	1	H	NHC ₂ H ₅	mp. 135-137.5°C
69		H	1	H	NHC ₂ H ₅	
70		H	1	H	NHC ₂ H ₅	²⁰ n _D 1.5756
71		H	1	CH ₃	NHC ₂ H ₅	

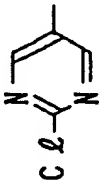
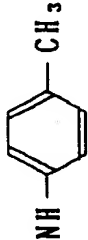
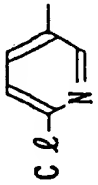
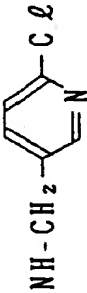
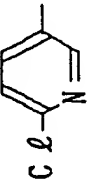
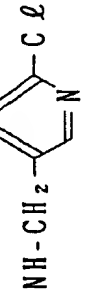
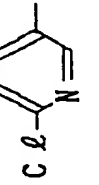
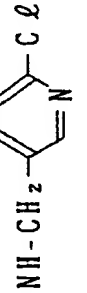
Comp No.	Z	R ¹	m	R ²	R ³	Physical property
72		H	1	H	NHC ₃ H ₇ -n	
73		H	1	C ₄ H ₉ -n	NHC ₃ H ₇ -n	
74		H	1	H	NHC ₃ H ₇ -iso	
75		H	1	CH ₃	NHC ₃ H ₇ -iso	

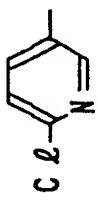
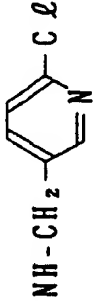
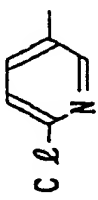
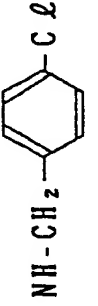
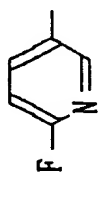
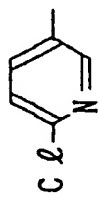
Comp No.	Z	R ¹	m	R ²	R ³	Physical property
76		H	1	H	$\text{NHC}_4\text{H}_9 - n$	
77		H	1	CH_3	$\text{NHC}_4\text{H}_9 - n$	
78		H	1	H	$\text{NHCH}_2\text{CH}_2(\text{OCH}_3)_2$	
79		H	1	H	NHCH_2CF_3	

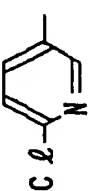
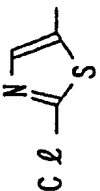
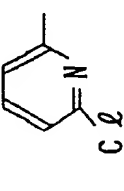
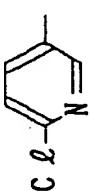
Comp No.	Z	R ¹	m	R ²	R ³	Physical property
80		H	1	CH ₃	NHCH ₂ CF ₃	
81		H	1	H	NHCH ₂ CH=CH ₂	
82		H	1	CH ₃	NHCH ₂ CH=CH ₂	
83		H	1	H	NHCH ₂ CH=CH ₂	


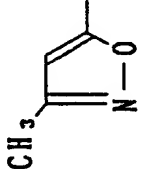
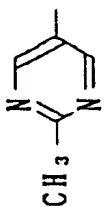
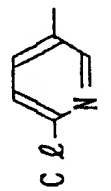
Comp No.	Z	R ¹	m	R ²	R ³	Physical property
84		H	1	H	$\text{NHCH}_2\text{C}\equiv\text{CH}$	
85		H	1	H	NHCH_2CN	
86		H	1	H	NHCH_2CN	
87		H	1	CH_3	NHCH_2CN	

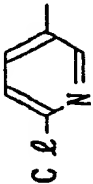
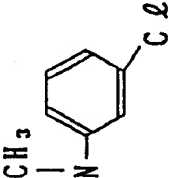
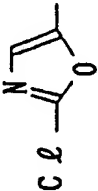
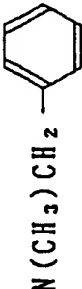
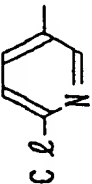
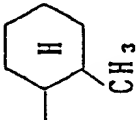
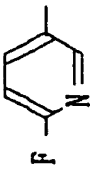
Comp No.	Z	R ¹	m	R ²	R ³	Physical property
88		H	1	H	NHCH ₂ CH ₂ CN	
89		H	1	H	NHCH ₂ CH ₂ NHCH ₃	
90		H	1	CH ₃	NHCH ₂ CH ₂ N(CH ₃) ₂	
91		H	1	CH ₃		

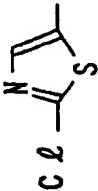
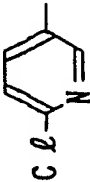

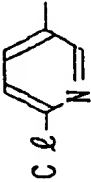
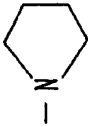
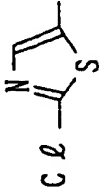
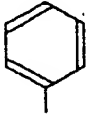
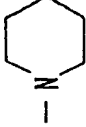
Comp. No.	Z	R ¹	m	R ²	R ³	Physical property
92		H	1	H		mp. 149-153°C
93		H	1	H		
94		CH ₃	1	H		
95		H	1	CH ₃		mp. 123-128°C

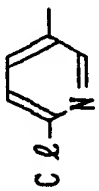
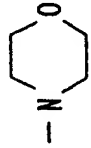
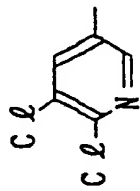

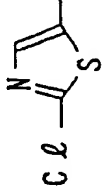
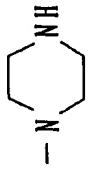
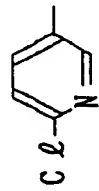
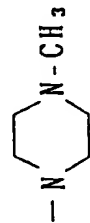
Comp No.	Z	R ¹	m	R ²	R ³	Physical property
96		CH ₃	1	CH ₃	 NH-CH ₂ -	mp. 217-221°C
97		H	1	H	 NH-CH ₂ -	
98		H	1	CH ₃	N(CH ₃) ₂	n _D ²⁰ 1.5703
99		H	1	H	N(CH ₃) ₂	

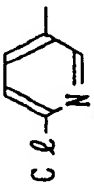
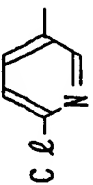
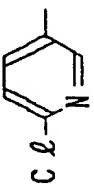
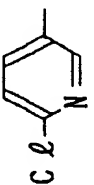
Comp No.	Z	R ¹	m	R ²	R ³	Physical property
100		—	0	H	N(CH ₃) ₂	
101		H	1	H	N(CH ₃) ₂	
102		H	1	H	N(CH ₃) ₂	
103		H	1	CH ₂ C≡CH	N(CH ₃) ₂	

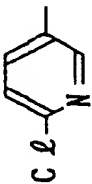
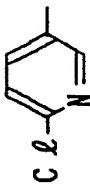
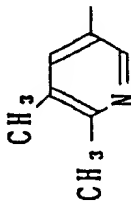
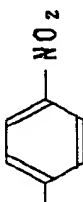
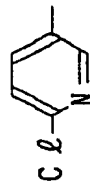
Comp. No.	Z	R ¹	m	R ²	R ³	Physical property
104		H	1	H	$N(CH_3)C_2H_5$	
105		H	1	H	$N(CH_3)C_3H_7-n$	
106		H	1	CH ₃	$N(CH_3)CH_2CH=CH$	
107		H	1	H	$N(CH_3)CH_2C \equiv CH$	

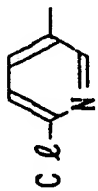
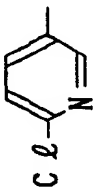
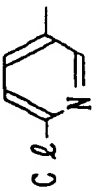
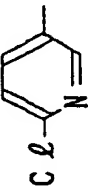
Comp No.	Z	R ¹	m	R ²	R ³	Physical property
108		CH ₃	1	H		
109		H	1	H		
110		H	1		N(C ₂ H ₅) ₂	
111		H	1	H	N(C ₂ H ₅) ₂	


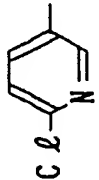
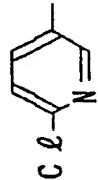
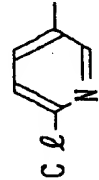
Comp. No.	Z	R ¹	m	R ²	R ³	Physical property
112		—	0	H	$N(C_2H_5)_2$	
113		H	1	H		
114		H	1	H		
115		H	1			

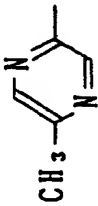
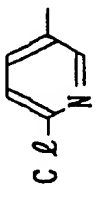
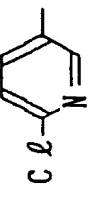
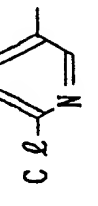
Comp No.	Z	R ¹	m	R ²	R ³	Physical property
116		H	1	H		
117		H	1	H		
118		H	1	CH ₃		
119		H	1	H		

Comp No.	Z	R ¹	m	R ²	R ³	Physical property
120		H	1	CH ₃	NHOCH ₃	
121		H	1	H	NHNH ₂	
122		H	1	CH ₃	NHNHCH ₃	
123		H	1	H	NHN(CH ₃) ₂	

Comp. No.	Z	R ¹	m	R ²	R ³	Physical property
124		H	1	CH ₃	NHOH	
125		H	1	H	$\begin{array}{c} \text{C}\ell \\ \\ \text{NHCH}_2\text{C}=\text{CH}_2 \end{array}$	
126		H	1		NHCH ₃	
127		CN	1	H	SCH ₃	

Comp. No.	Z	R ¹	m	R ²	R ³	Physical property
128		CN	1	CH ₃	SCH ₃	
129		CN	1	H	OCH ₃	
130		CN	1	H	NHCH ₃	
131		H	1	CH ₂ CH=CHC ₂ H ₅	SCH ₃	

Comp No.	Z	R ¹	m	R ²	R ³	Physical property
132		H	1	H	NHC ₄ H ₉ -n	
133		H	1	H	NHCH ₂ CH ₂ OH	
134		H	1	CH ₃	NHCH ₂ CH ₂ SH	
135		H	1	CH ₃	NHCH ₂ CH ₂ NH ₂	

Comp No.	Z	R ¹	m	R ²	R ³	Physical property
136		H	1	H	NHCH ₂ CH ₂ Cℓ	
137		H	1	CH ₃	NH(CH ₂) ₃ COOH	
138		H	1	H	NHCOOCH ₃	
139		H	1	C ₂ H ₅	NHCOOC ₂ H ₅	

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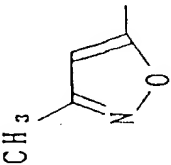
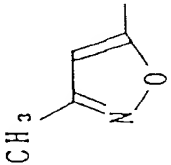
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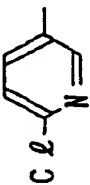
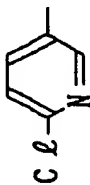
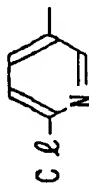
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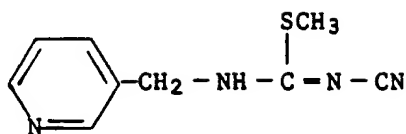
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Comp. No.	Z	R ¹	m	R ²	R ³	Physical property
142		H	1	H	SCH ₃	
143		H	1	CH ₃	SCH ₃	

Comp No.	Z	R ¹	m	R ²	R ³	Physical property
144		H	1	CH ₃	NHC ₃ H ₇ -n	
145		H	1	H	NHCH ₂ CH ₂ SCH ₃	
146		H	1	H	$\begin{array}{c} \text{CH}_3 \\ \\ \text{NCH}_2\text{CH}_2\text{SCH}_3 \end{array}$	

Biological Test:-

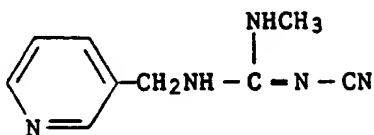
Comparative compound E-1



(disclosed in Japanese Patent
Laid-open No. 233903/1988)

15 (disclosed in Japanese Patent Laid-open No. 233903/1988)

Comparative compound E-2



(disclosed in Japanese Patent
Laid-open No. 47766/1989)

30 (disclosed in Japanese Patent Laid-open No. 47766/1989)

Example 6:

35 Test on Nephotettix cincticeps having resistance to organophosphorus agents:-

Preparation of a test chemical

Solvent: 3 parts by weight of xylene

40 Emulsifier: 1 part by weight of polyoxyethylene alkyl phenyl ether

To form a suitable preparation, 1 part by weight of the active compound was mixed with the aforesaid amount of the solvent containing the aforesaid amount of the emulsifier. The mixture was diluted with water to a predetermined concentration.

45 Testing method

Onto rice plants, about 10 cm tall, planted in pots each having a diameter of 12 cm was sprayed 10 ml per pot of the water-dilution of each active compound in a predetermined concentration prepared as above. The sprayed chemical was dried, and a wire net having a diameter of 7 cm and a height of 14 cm was put
50 over each pot, and 30 female imagoes of Nephotettix cincticeps showing resistance to organophosphorus agents were released into the net. The pots were each placed in a constant temperature chamber and the number of dead insects was examined 2 days later, and the insect mortality was calculated.

The results are shown in Table 2.

Table 2

Compound No.	Concentration of the active ingredient ppm	Insect mortality, %
1	50	100
10	50	100
62	50	100
63	50	100
99	50	100
Comparative E-1	50	0
E-2	50	20

Example 7:

Test on planthoppers:-

Testing method

A water dilution in a predetermined concentration of the active compound prepared as in Example 6 was sprayed onto rice plants, about 10 cm tall, grown in pots with a diameter of 12 cm in an amount of 10 ml per pot. The sprayed chemical was dried, and a wire net, 7 cm in diameter and 14 cm tall, was put over each of the pots. Thirty female imagoes of Nilaparvata lugens Stal of a strain which showed resistance to organophosphorus chemicals were released into the net. The pots were left to stand in a constant temperature chamber and the number of dead insects was examined two days later. The insect mortality was then calculated.

In the same way as above, the kill ratio was calculated on Sogatella furcifera Horvath and organophosphorus-resistant Laodelphax striatellus Fallen.

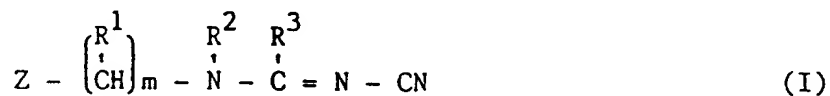
The results are shown in Table 3.

Table 3

Compound No.	Concentration of the active ingredient ppm	Insect mortality, %		
		Nilaparvata lugens	Laodelphax striatellus	Sogatella furcifera
1	50	100	100	100
62	50	100	100	100
63	50	100	100	100
99	50	100	100	100
Comparative				
E-1	50	0	0	0
E-2	50	0	0	0

Claims

- Use of cyano compounds of the formula (I)



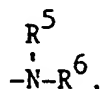
wherein R¹ is hydrogen, cyano or C₁₋₄ alkyl,

m is 0 or 1,

R² is hydrogen, C₁₋₆ alkyl, C₃₋₄ alkenyl optionally substituted by halogen,

C₃₋₄ alkynyl, C₃₋₈ cycloalkyl optionally substituted by methyl, optionally halogen-substituted phenyl, optionally halogen-substituted benzyl, hydroxy, C₁₋₄ alkoxy or -CH₂-Z, in which Z has the same meanings as stated below,

R³ is -O-R⁴, -S-R⁴ or



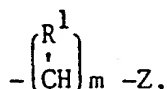
in which R⁴ is C₁₋₆ alkyl, C₃₋₄ alkenyl,

C₃₋₄ alkynyl, C₃₋₈ cycloalkyl, optionally halogen-substituted phenyl, optionally halogen-substituted benzyl or -(CH₂)_n-Z, in which n is 1 or 2 and

Z has the same meanings as stated below, and

R⁵ and R⁶ are hydrogen, C₁₋₉ alkyl optionally substituted by at least one selected from a group consisting of halogen, hydroxy, mercapto, C₁₋₂ alkoxy, C₁₋₂ alkylthio,

C₃₋₆ cycloalkyl, amino, C₁₋₂ monoalkylamino,
 C₂₋₄ (in total) di-alkylamino, carboxy, C₁₋₂ alkoxy-carbonyl and cyano, C₃₋₄ alkenyl optionally substituted by halogen,
 C₃₋₄ alkynyl, optionally chlorine substituted phenyl, optionally chlorine substituted benzyl, C₁₋₄ alkoxy,
 hydroxy, formyl, C₁₋₄ alkoxy-carbonyl, C₁₋₄ alkylamino, C₂₋₄ (in total) di-alkylamino, amino, acyl or



in which R¹ and m have the same meanings as stated above, and Z has the same meanings as stated below, and in addition,

R⁵ and R⁶ may form, together with the N-atom to which they are bonded, a 3 to 7 membered ring which may be substituted by C₁₋₂ alkyl and may contain N, O or S as the member of said ring, besides the N-atom to which they are bonded, and

Z is a 5 membered heterocyclic group which is substituted by halogen or C₁₋₂ alkyl and contains one or two nitrogen atoms, or one nitrogen atom and either one oxygen atom or one sulfur atom, or a 6 membered heterocyclic group which is substituted by halogen or C₁₋₂ alkyl and contains one or two nitrogen atoms,

provided that where Z is pyridyl substituted by halogen, m is 1, R² is C₁₋₆ alkyl and R³ is -S-alkyl-(C₁₋₆) or -S-benzyl, then R¹ is cyano or C₁₋₄ alkyl for combating harmful insects.

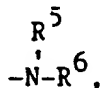
2. Use of compounds of the formula (I) according to claim 1 wherein

R¹ is hydrogen or C₁₋₃ alkyl,

m is 0 or 1,

R² is hydrogen, C₁₋₄ alkyl, allyl, propargyl, phenyl optionally substituted by halogen, benzyl optionally substituted by halogen, hydroxy, C₁₋₃ alkoxy or -CH₂-Z¹ in which Z¹ is pyridyl optionally substituted by halogen,

R³ is -O-R⁴, -S-R⁴ or



in which

R⁴ is C₁₋₄ alkyl, allyl, propargyl, C₃₋₆ cycloalkyl, phenyl optionally substituted by halogen, benzyl optionally substituted by halogen or -CH₂-Z¹ in which

Z¹ has the same meaning as stated above,

R⁵ and R⁶ are hydrogen, C₁₋₉ alkyl optionally substituted by fluorine or chlorine, allyl optionally substituted by chlorine, propargyl, phenyl optionally substituted by chlorine, benzyl optionally substituted by chlorine, C₁₋₃ alkoxy, hydroxy, hydroxy-C₁₋₂ alkyl, mercapto-C₁₋₂ alkyl, amino-C₁₋₂ alkyl, C₁₋₃ alkylamino, dimethylamino, amino, cyano-C₁₋₂ alkyl, pyridyl optionally substituted by chlorine or methyl, or -CH₂-Z² in which Z² is pyridyl optionally substituted by halogen or 5-thiazolyl optionally substituted by halogen,

and in addition,

R⁵ and R⁶ may form, together with the N-atom to which they are bonded, a 3 to 6 membered ring which may be substituted by methyl and may contain N, O or S as the member of said ring, besides the N-atom to which they are bonded, and

Z is a 5 membered heterocyclic group which is substituted by halogen or C₁₋₂ alkyl and contains one or two nitrogen atoms, or one nitrogen atom and either one oxygen atom or one sulfur atom, or a 6 membered heterocyclic group which is substituted by halogen or

C₁₋₂ alkyl and contains one or two nitrogen atoms, provided that where Z is pyridyl substituted by halogen, m is 1, R² is C₁₋₄ alkyl and

R³ is -S-alkyl-(C₁₋₄) or -S-benzyl, then R¹ is C₁₋₃ alkyl for combating harmful insects.

3. Use of compounds of the formula (I) according to claim 1 wherein
 R¹ is hydrogen, methyl, ethyl or propyl,
 m is 0 or 1
 R² is hydrogen, methyl, ethyl, propyl, allyl, propargyl, phenyl optionally substituted by chlorine,
 hydroxy, methoxy, ethoxy or pyridylmethyl optionally substituted by chlorine,
 R³ is -O-R⁴, -S-R⁴ or



in which

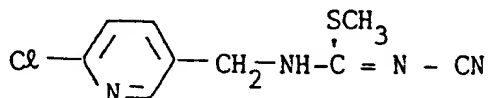
R⁴ is C₁₋₃ alkyl, allyl, propargyl, cyclohexyl, phenyl, benzyl optionally substituted by chlorine, pyridylmethyl optionally substituted by chlorine,

R⁵ and R⁶ are hydrogen, C₁₋₄ alkyl optionally substituted by fluorine or chlorine, allyl optionally substituted by chlorine, propargyl, phenyl optionally substituted by chlorine, benzyl optionally substituted by chlorine, methoxy, hydroxy, hydroxyethyl, C₁₋₂ alkylamino, dimethylamino, amino, cyanoethyl, 2-chloro-5-pyridylmethyl or 2-chloro-5-thiazolylmethyl, and in addition,

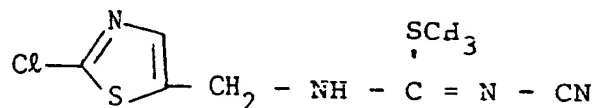
R⁵ and R⁶ may form, together with the N-atom to which they are bonded, pyrrolidino, piperidino, 2-methylpiperidino, morpholino, piperazino or isoxazolidino, and Z is a 5 membered heterocyclic group which is substituted by halogen or C₁₋₂ alkyl and contains one or two nitrogen atoms, or one nitrogen atom and either one oxygen atom or one sulfur atom, or a 6 membered heterocyclic group which is substituted by halogen or C₁₋₂ alkyl and contains one or two nitrogen atoms, provided that where Z is pyridyl substituted by halogen, m is 1,

R² is methyl, ethyl or propyl and R³ is -S-alkyl(C₁₋₃) or -S-benzyl, then R¹ is methyl, ethyl or propyl for combating harmful insects.

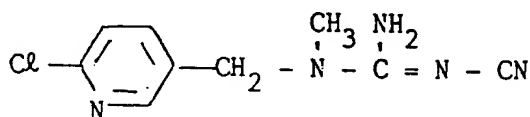
4. Use of compounds according to claim 1, wherein such compound is
 S-methyl-N-(2-chloro-5-pyridylmethyl)-N'-cyanoisothiourea of the following formula:



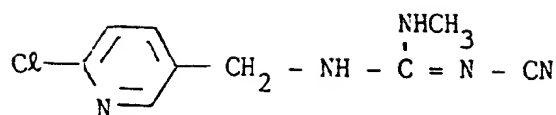
S-methyl-N-(2-chloro-5-thiazolylmethyl)-N'-cyanoisothiourea of the following formula:



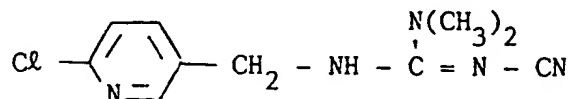
3-(2-chloro-5-pyridylmethyl)-3-methyl-2-cyanoguanidine of the following formula:



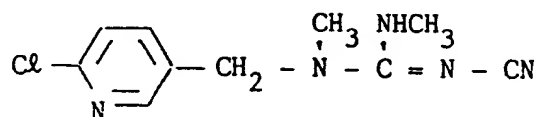
3-(2-chloro-5-pyridylmethyl)-1-methyl-2-cyanoguanidine of the following formula:



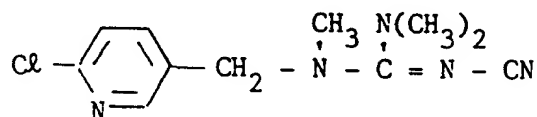
3-(2-chloro-5-pyridylmethyl)-1,1-dimethyl-2-cyanoguanidine of the following formula:



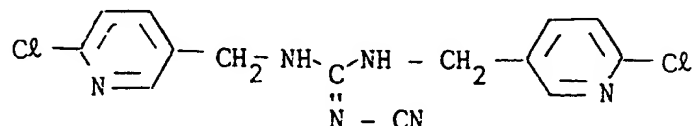
3-(2-chloro-5-pyridylmethyl)-1,3-dimethyl-2-cyanoguanidine of the following formula:



3-(2-chloro-5-pyridylmethyl)-1,1,3-trimethyl-2-cyanoguanidine of the following formula:

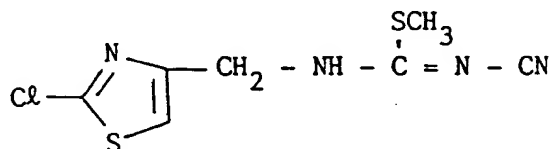


1,3-bis(2-chloro-5-pyridylmethyl)-2-cyanoguanidine of the following formula;



and

S-methyl-N-(2-chloro-5-thiazolylmethyl)-N'-cyanoisothiourea of the following formula:

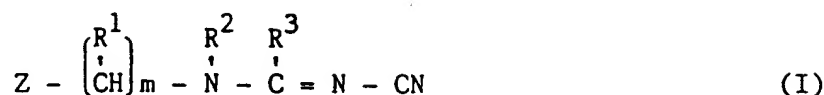


to combat harmful insects.

5. Insecticidal compositions, characterised in that they contain at least one cyano compound of the formula (I) according to claim 1.

6. Process for the preparation of insecticidal compositions, characterised in that cyano compounds of the formula (I) according to claim 1 are mixed with extenders and/or surface-active agents.

7. Cyano compounds of the formula (I)



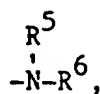
wherein R¹ is hydrogen, cyano or C₁₋₄ alkyl,

m is 1,

R² is hydrogen, C₁₋₆ alkyl, C₃₋₄ alkenyl optionally substituted by halogen,

C₃₋₄ alkynyl, C₃₋₈ cycloalkyl optionally substituted by methyl, optionally halogen-substituted phenyl, optional halogen-substituted benzyl, hydroxy, C₁₋₄ alkoxy or -CH₂-Z, in which Z has the same meanings as stated below,

R³ is -O-R⁴, -S-R⁴ or



in which R⁴ is C₁₋₆ alkyl, C₃₋₄ alkenyl,

C₃₋₄ alkynyl, C₃₋₈ cycloalkyl, optionally halogen-substituted phenyl, optionally halogen-substituted benzyl or -(CH₂)_n-Z, in which n is 1 or 2 and

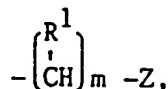
Z has the same meanings as stated below, and

R⁵ and R⁶ are hydrogen, C₁₋₉ alkyl optionally substituted by at least one selected from a group consisting of halogen, hydroxy, mercapto, C₁₋₂ alkoxy, C₁₋₂ alkylthio,

C₃₋₆ cycloalkyl, amino, C₁₋₂ monoalkylamino,

C₂₋₄ (in total) di-alkylamino, carboxy, C₁₋₂ alkoxy-carbonyl and cyano, C₃₋₄ alkenyl optionally substituted by halogen,

C₃₋₄ alkynyl, optionally, chlorine-substituted phenyl, optionally chlorine substituted benzyl, C₁₋₄ alkoxy, hydroxy, formyl, C₁₋₄ alkoxy-carbonyl, C₁₋₄ alkylamino, C₂₋₄ (in total) di-alkylamino, amino, acyl or



in which R¹ and m have the same meanings as stated above, and Z has the same meanings as stated below, and in addition,

R⁵ and R⁶ may form, together with the N-atom to which they are bonded, a 3 to 7 membered ring which may be substituted by C₁₋₂ alkyl and may contain N, O or S as the member of said ring, besides the N-atom to which they are bonded, and

Z is a 5 membered heterocyclic group which is substituted by halogen or C₁₋₂ alkyl and contains one or two nitrogen atoms, or one nitrogen atom and either one oxygen atom or one sulfur atom, or a 6 membered heterocyclic group which is substituted by halogen or C₁₋₂ alkyl and contains one or two nitrogen atoms,

provided that where Z is pyridyl substituted by halogen, m is 1, R² is C₁₋₆ alkyl and R³ is S-alkyl(C₁₋₆) or -S-benzyl, then R¹ is cyano or C₁₋₄ alkyl and furthermore with the exception of N-cyano-N'-methyl-N''-[(4-methyl-thiazol-2-yl)methyl]guanidine

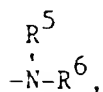
8. The compounds of the formula (I) according to claim 7 wherein

R¹ is hydrogen, methyl, ethyl or propyl,

m is 1

R² is hydrogen, methyl, ethyl, propyl, allyl, propargyl, phenyl optionally substituted by chlorine, hydroxy, methoxy, ethoxy or pyridylmethyl optionally substituted by chlorine,

R³ is -O-R⁴, -S-R⁴ or



in which

R^4 is C_{1-3} alkyl, allyl, propargyl, cyclohexyl, phenyl, benzyl optionally substituted by chlorine, pyridylmethyl optionally substituted by chlorine,

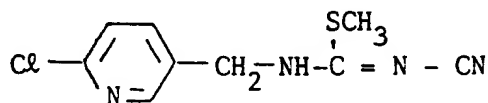
R^5 and R^6 are hydrogen, C_{1-4} alkyl optionally substituted by fluorine or chlorine, allyl optionally substituted by chlorine, propargyl, phenyl optionally substituted by chlorine, benzyl optionally substituted by chlorine, methoxy, hydroxy, hydroxyethyl, C_{1-2} alkylamino, dimethylamino, amino, cyanoethyl, 2-chloro-5-pyridylmethyl or 2-chloro-5-thiazolylmethyl, and in addition,

R^5 and R^6 may form, together with the N-atom to which they are bonded, pyrrolidino, piperidino, 2-methylpiperidino, morpholino, piperazino or isoxazolidino, and Z is a 5 membered heterocyclic group which is substituted by halogen or C_{1-2} alkyl and contains one or two nitrogen atoms, or one nitrogen atom and either one oxygen atom or one sulfur atom, or a 6 membered heterocyclic group which is substituted by halogen or C_{1-2} alkyl and contains one or two nitrogen atoms, provided that where Z is pyridyl substituted by halogen, m is 1,

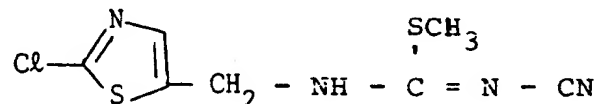
R^2 is methyl, ethyl or propyl and R^3 is -S-alkyl(C_{1-3}) or -S-benzyl, then R^1 is methyl, ethyl or propyl and

furthermore with the exception of N-cyano-N'-methyl-N''-[(4-methyl-thiazol-2-yl)methyl]guanidine.

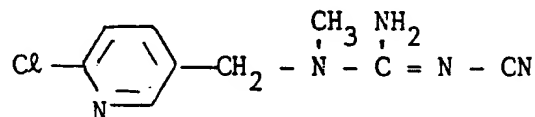
9. Compounds according to claim 7, wherein such compound is S-methyl-N-(2-chloro-5-pyridylmethyl)-N'-cyanoisothiourea of the following formula:



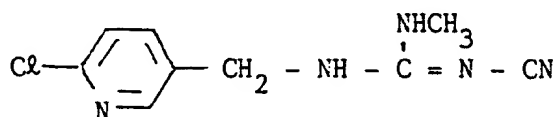
S-methyl-N-(2-chloro-5-thiazolylmethyl)-N'-cyanoisothiourea of the following formula:



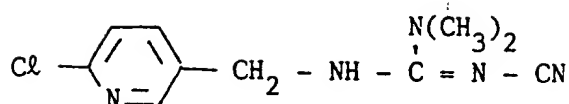
3-(2-chloro-5-pyridylmethyl)-3-methyl-2-cyanoguanidine of the following formula:



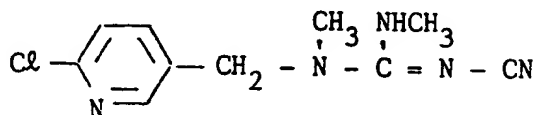
3-(2-chloro-5-pyridylmethyl)-1-methyl-2-cyanoguanidine of the following formula:



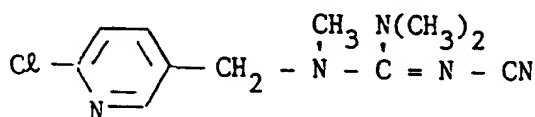
3-(2-chloro-5-pyridylmethyl)-1,1-dimethyl-2-cyanoguanidine of the following formula:



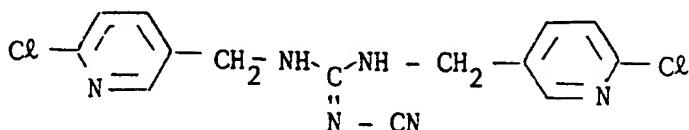
3-(2-chloro-5-pyridylmethyl)-1,3-dimethyl-2-cyanoguanidine of the following formula:



3-(2-chloro-5-pyridylmethyl)-1,1,3-trimethyl-2-cyanoguanidine of the following formula:

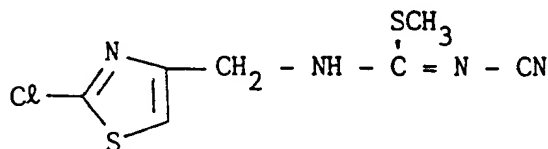


1,3-bis(2-chloro-5-pyridylmethyl)-2-cyanoguanidine of the following formula;

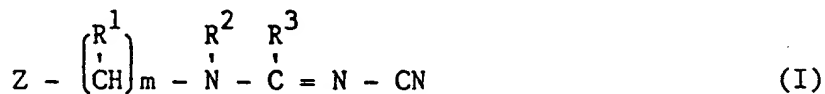


and

S-methyl-N-(2-chloro-5-thiazolylmethyl)-N'-cyanoisothiourea of the following formula:



10. Process for the preparation of cyano compounds of the formula (I) according to claim 7



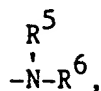
wherein R¹ is hydrogen, cyano or C₁₋₄ alkyl,

m is 1,

R² is hydrogen, C₁₋₆ alkyl, C₃₋₄ alkenyl optionally substituted by halogen,

C₃₋₄ alkynyl, C₃₋₈ cycloalkyl optionally substituted by methyl, optionally halogen-substituted phenyl, optionally halogen-substituted benzyl, hydroxy, C₁₋₄ alkoxy or -CH₂-Z, in meanings as stated below,

R³ is -O-R⁴, -S-R⁴

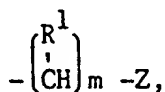


in which R⁴ is C₁₋₆ alkyl, C₃₋₄ alkenyl, C₃₋₄ alkynyl, C₃₋₈ cycloalkyl, optionally halogen-substituted phenyl, optionally halogen-substituted benzyl or -(CH₂)_n-Z, in which n is 1 or 2 and Z has the same meanings as stated below, and

R⁵ and R⁶ are hydrogen, C₁₋₉ alkyl optionally substituted by at least one selected from a group consisting of halogen, hydroxy, mercapto, C₁₋₂ alkoxy, C₁₋₂ alkylthio,

C₃₋₆ cycloalkyl, amino, C₁₋₂ monoalkylamino, C₂₋₄ (in total)di-alkylamino, carboxy, C₁₋₂ alkoxy-carbonyl and cyano, C₃₋₄ alkenyl optionally substituted by halogen,

C₃₋₄ alkynyl, optionally chlorine-substituted phenyl, optionally chlorine substituted benzyl, C₁₋₄ alkoxy, hydroxy, formyl, C₁₋₄ alkoxy-carbonyl, C₁₋₄ alkylamino, C₂₋₄ (in total)di-alkylamino, amino, acyl or



in which R¹ and m have the same meanings as stated above, and Z has the same meanings as stated below, and in addition,

R⁵ and R⁶ may form, together with the N-atom to which they are bonded, a 3 to 7 membered ring which may be substituted by C₁₋₂ alkyl and may contain N, O or S as the member of said ring, besides the N-atom to which they are bonded, and

provided that where Z is pyridyl substituted by halogen, m is 1, R² is C₁₋₆ alkyl and R³ is S-alkyl(C₁₋₆) or -S-benzyl, then R¹ is cyano or C₁₋₄ alkyl and furthermore with the exception of

N-cyano-N'-methyl-N''-[(4-methyl-thiazol-2-yl)methyl]guanidine characterised in that

a) in the case where R³ is -S-R⁴;
compounds of the formula (II)



wherein R¹, m, R² and Z have the same meanings as stated above, are reacted with compounds of the formula (III)



wherein R⁴ has the same meaning as stated above, in the presence of inert solvents,

or

b) in the case where R³ is -O-R⁴;

the aforesaid compounds of the formula (II) are reacted with compounds of the formula (IV)



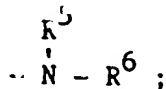
5

wherein R⁴ has the same meaning as stated above,
in the presence of inert solvents,

or

10

c) in the case where R³ is



15

the aforesaid compounds of the formula (II) are reacted with compounds of the formula (V)

20



25

wherein R⁴, R⁵ and R⁶ have the same meanings as stated above,
in the presence of inert solvents,

or

d) in the case where R³ is - S - R⁴ and m is 1;
compounds of the formula (VI)

30



35

wherein R¹ and Z have the same meanings as stated above, and M is halogen,
are reacted with compounds of the formula (VII)

40



45

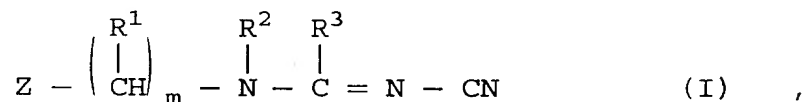
wherein R² and R⁴ have the same meanings as stated above,
in the presence of inert solvents and if appropriate in the presence of a base.

Patentansprüche

50

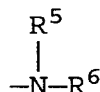
1. Verwendung von Cyan-Verbindungen der Formel (I)

55

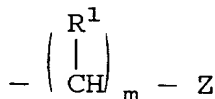


worin

R¹ Wasserstoff, Cyan oder C₁₋₄-Alkyl ist,
 m 0 oder 1 ist,
 R² Wasserstoff, C₁₋₆-Alkyl, C₃₋₄-Alkenyl, das gegebenenfalls durch Halogen substituiert
 ist, C₃₋₄-Alkynyl, C₃₋₈-Cycloalkyl, das gegebenenfalls durch Methyl substituiert ist,
 5 gegebenenfalls durch Halogen substituiertes Phenyl, gegebenenfalls durch Halogen
 substituiertes Benzyl, Hydroxy, C₁₋₄-Alkoxy oder -CH₂-Z ist worin Z die gleichen
 Bedeutungen hat, wie sie unten angegeben sind,
 R³ -O-R⁴, -S-R⁴, oder



ist, worin
 R⁴ C₁₋₆-Alkyl, C₃₋₄-Alkenyl, C₃₋₄-Alkynyl, C₃₋₈-Cycloalkyl, gegebenenfalls durch Halo-
 gen substituiertes Phenyl, gegebenenfalls durch Halogen substituiertes Benzyl oder
 -(CH₂)_n-Z ist, worin n 1 oder 2 ist und Z die gleichen Bedeutungen hat, wie sie unten
 angegeben sind, und
 20 R⁵ und R⁶ Wasserstoff, C₁₋₉-Alkyl, das gegebenenfalls durch wenigstens einen Substituenten,
 ausgewählt aus der aus Halogen, Hydroxy, Mercapto, C₁₋₂-Alkoxy, C₁₋₂-Alkylthio,
 C₃₋₆-Cycloalkyl, Amino, C₁₋₂-Monoalkylamino, C₂₋₄ (insgesamt)-Dialkylamino, Car-
 boxy, C₁₋₂-Alkoxy-carbonyl und Cyan bestehenden Gruppe, substituiert ist, C₃₋₄-
 Alkenyl, das gegebenenfalls durch Halogen substituiert ist, C₃₋₄-Alkynyl, gegebenen-
 25 falls durch Chlor substituiertes Phenyl, gegebenenfalls durch Chlor substituiertes
 Benzyl C₁₋₄-Alkoxy, Hydroxy, Formyl, C₁₋₄-Alkoxy-carbonyl, C₁₋₄-Alkylamino, C₂₋₄-
 (insgesamt)-Dialkylamino, Amino, Acyl oder



sind, worin
 35 R¹ und m die oben angegebenen Bedeutungen haben und Z die gleichen Bedeutungen
 hat, wie sie unten angegeben sind, und außerdem
 R⁵ und R⁶ zusammen mit dem N-Atom, an das sie gebunden sind, einen 3- bis 7-gliedrigen Ring
 bilden können, der durch C₁₋₂-Alkyl substituiert sein kann und N, O oder S als Glied
 des Ringes neben dem N-Atom, an das sie gebunden sind, enthalten kann, und
 40 Z eine 5-gliedrige heterocyclische Gruppe, die durch Halogen oder C₁₋₂-Alkyl substitu-
 iert ist und ein oder zwei Stickstoff-Atome oder ein Stickstoff-Atom und entweder ein
 Sauerstoff-Atom oder ein Schwefel-Atom enthält, oder
 eine 6-gliedrige heterocyclische Gruppe, die durch Halogen oder C₁₋₂-Alkyl substitu-
 iert ist und ein oder zwei Stickstoff-Atome ist, mit der Maßgabe ist, daß,

45 wenn
 Z durch Halogen substituiertes Pyridyl ist,
 m 1 ist,
 R² C₁₋₆-Alkyl ist und
 R³ -S-Alkyl(C₁₋₆) oder -S-Benzyl ist,

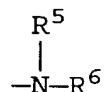
50 dann
 R¹ Cyan oder C₁₋₄-Alkyl ist,
 zur Bekämpfung schädlicher Insekten.

2. Verwendung von Verbindungen der Formel (I) nach Anspruch 1, worin

55 R¹ Wasserstoff oder C₁₋₃-Alkyl ist,
 m 0 oder 1 ist,
 R² Wasserstoff, C₁₋₄-Alkyl, Allyl, Propargyl, gegebenenfalls durch Halogen substituiertes
 Phenyl, gegebenenfalls durch Halogen substituiertes Benzyl, Hydroxy, C₁₋₃-Alkoxy

oder $-\text{CH}_2\text{-Z}^1$ ist, worin Z^1 Pyridyl ist, das gegebenenfalls durch Halogen substituiert ist,

R^3 $-\text{O-R}^4$, $-\text{S-R}^4$, oder



ist, worin

R^4 C_{1-4} -Alkyl, Allyl, Propargyl, C_{3-6} -Cycloalkyl, gegebenenfalls durch Halogen substituiertes Phenyl, gegebenenfalls durch Halogen substituiertes Benzyl oder $-\text{CH}_2\text{-Z}^1$ ist, worin Z^1 die oben angegebenen Bedeutungen hat,

R^5 und R^6 Wasserstoff, C_{1-9} -Alkyl, das gegebenenfalls durch Fluor oder Chlor substituiert ist, Allyl, das gegebenenfalls durch Chlor substituiert ist, Propargyl, gegebenenfalls durch Chlor substituiertes Phenyl, gegebenenfalls durch Chlor substituiertes Benzyl, C_{1-3} -Alkoxy, Hydroxy, Hydroxy- $_{1-2}$ -Alkyl, Mercapto- $_{1-2}$ -Alkyl, Amino- C_{1-2} -alkyl, C_{1-3} -Alkylamino, Dimethylamino, Amino, Cyan- C_{1-2} -alkyl, Pyridyl, das gegebenenfalls durch Chlor oder Methyl substituiert ist, oder $-\text{CH}_2\text{-Z}^2$, worin Z^2 Pyridyl, das gegebenenfalls durch Halogen substituiert ist, oder 5-Thiazolyl, das gegebenenfalls durch Halogen substituiert ist, sind, und außerdem

R^5 und R^6 zusammen mit dem N-Atom, an das sie gebunden sind, einen 3- bis 6-gliedrigen Ring bilden können, der durch Methyl substituiert sein kann und N, O oder S als Glied des Ringes neben dem N-Atom, an das sie gebunden sind, enthalten kann, und

Z eine 5-gliedrige heterocyclische Gruppe, die durch Halogen oder C_{1-2} -Alkyl substituiert ist und ein oder zwei Stickstoff-Atome oder ein Stickstoff-Atom und entweder ein Sauerstoff-Atom oder ein Schwefel-Atom enthält, oder eine 6-gliedrige heterocyclische Gruppe, die durch Halogen oder C_{1-2} -Alkyl substituiert ist und ein oder zwei Stickstoff-Atome ist, mit der Maßgabe ist, daß,

wenn Z durch Halogen substituiertes Pyridyl ist,

m 1 ist,

R^2 C_{1-4} -Alkyl ist und

R^3 $-\text{S-Alkyl}(\text{C}_{1-4})$ oder $-\text{S-Benzyl}$ ist,

dann

R^1 C_{1-3} -Alkyl ist,

zur Bekämpfung schädlicher Insekten.

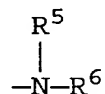
3. Verwendung von Verbindungen der Formel (I) nach Anspruch 1, worin

R^1 Wasserstoff, Methyl, Ethyl oder Propyl ist,

m 0 oder 1 ist,

R^2 Wasserstoff, Methyl, Ethyl, Propyl, Allyl, Propargyl, gegebenenfalls durch Chlor substituiertes Phenyl, Hydroxy, Methoxy, Ethoxy oder Pyridylmethyl ist, das gegebenenfalls durch Chlor substituiert ist,

R^3 $-\text{O-R}^4$, $-\text{S-R}^4$, oder



ist, worin

R^4 C_{1-3} -Alkyl, Allyl, Propargyl, Cyclohexyl, Phenyl, gegebenenfalls durch Chlor substituiertes Benzyl, gegebenenfalls durch Chlor substituiertes Pyridylmethyl ist,

R^5 und R^6 Wasserstoff, C_{1-4} -Alkyl, das gegebenenfalls durch Fluor oder Chlor substituiert ist, Allyl, das gegebenenfalls durch Chlor substituiert ist, Propargyl, gegebenenfalls durch Chlor substituiertes Phenyl, gegebenenfalls durch Chlor substituiertes Benzyl, Methoxy, Hydroxy, Hydroxyethyl, C_{1-2} -Alkylamino, Dimethylamino, Amino, Cyanethyl,

R⁵ und R⁶ 2-Chlor-5-pyridylmethyl oder 2-Chlor-5-thiazolylmethyl sind, und außerdem
 Z zusammen mit dem N-Atom, an das sie gebunden sind, Pyrrolidino, Piperidino, 2-Methyl-piperidino, Morpholino, Piperazino oder Isoxazolidino bilden können, und
 5 eine 5-gliedrige heterocyclische Gruppe, die durch Halogen oder C₁₋₂-Alkyl substituiert ist und ein oder zwei Stickstoff-Atome oder ein Stickstoff-Atom und entweder ein Sauerstoff-Atom oder ein Schwefel-Atom enthält, oder
 eine 6-gliedrige heterocyclische Gruppe, die durch Halogen oder C₁₋₂-Alkyl substituiert ist und ein oder zwei Stickstoff-Atome ist, mit der Maßgabe ist, daß,

wenn

Z durch Halogen substituiertes Pyridyl ist,

m 1 ist,

R² Methyl, Ethyl oder Propyl ist und

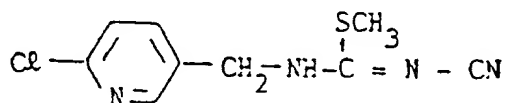
R³ -S-Alkyl(C₁₋₃) oder -S-Benzyl ist,

dann

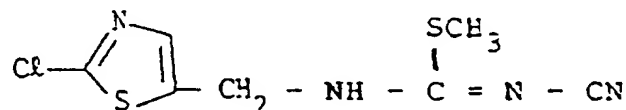
R¹ Methyl, Ethyl oder Propyl ist,

zur Bekämpfung schädlicher Insekten.

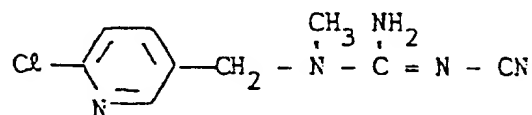
4. Verwendung der Verbindungen nach Anspruch 1, worin eine solche Verbindung
 S-Methyl-N-(2-chloro-5-pyridylmethyl)-N'-cyanisothioharnstoff der nachstehenden Formel



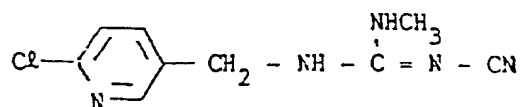
S-Methyl-N-(2-chloro-5-thiazolylmethyl)-N'-cyanisothioharnstoff der nachstehenden Formel



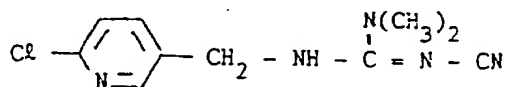
3-(2-Chlor-5-pyridylmethyl)-3-methyl-2-cyanguanidin der nachstehenden Formel



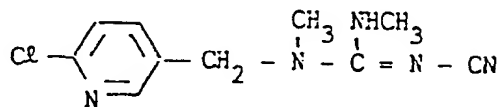
3-(2-Chlor-5-pyridylmethyl)-1-methyl-2-cyanguanidin der nachstehenden Formel



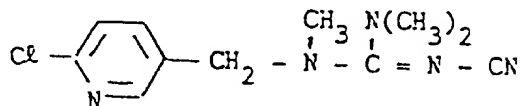
3-(2-Chlor-5-pyridylmethyl)-1,1-dimethyl-2-cyanguanidin der nachstehenden Formel



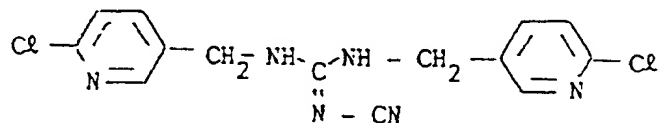
3-(2-Chlor-5-pyridylmethyl)-1,3-dimethyl-2-cyanguanidin der nachstehenden Formel



3-(2-Chlor-5-pyridylmethyl)-1,1,3-trimethyl-2-cyanguanidin der nachstehenden Formel

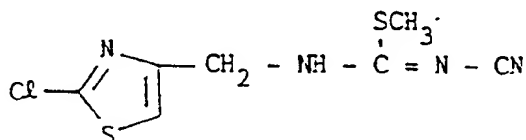


1,3-Bis-(2-chlor-5-pyridylmethyl)-2-cyanguanidin der nachstehenden Formel



und

S-Methyl-N-(2-chloro-5-thiazolylmethyl)-N'-cyanisothioharnstoff der nachstehenden Formel



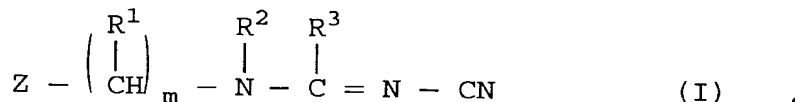
ist,

zur Bekämpfung schädlicher Insekten.

5. Insektizide Zusammensetzungen, dadurch gekennzeichnet, daß sie wenigstens eine Cyan-Verbindung der Formel (I) nach Anspruch 1 enthalten.

6. Verfahren zur Herstellung insektizider Zusammensetzungen, dadurch gekennzeichnet, daß Cyan-Verbindungen der Formel (I) nach Anspruch 1 mit Streckmitteln und/oder grenzflächenaktiven Mitteln vermischt werden.

7. Cyan-Verbindungen der Formel (I)



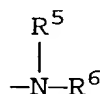
worin

R¹ Wasserstoff, Cyan oder C₁₋₄-Alkyl ist,

m 1 ist,

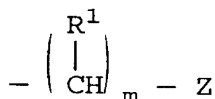
R² Wasserstoff, C₁₋₆-Alkyl, C₃₋₄-Alkenyl, das gegebenenfalls durch Halogen substituiert ist, C₃₋₄-Alkynyl, C₃₋₈-Cycloalkyl, das gegebenenfalls durch Methyl substituiert ist, gegebenenfalls durch Halogen substituiertes Phenyl, gegebenenfalls durch Halogen

substituiertes Benzyl, Hydroxy, C₁₋₄-Alkoxy oder -CH₂-Z ist, worin Z die gleichen Bedeutungen hat, wie sie unten angegeben sind,
 R³ -O-R⁴, -S-R⁴, oder



ist, worin
 R⁴ C₁₋₆-Alkyl, C₃₋₄-Alkenyl, C₃₋₄-Alkynyl, C₃₋₈-Cycloalkyl, gegebenenfalls durch Halogen substituiertes Phenyl, gegebenenfalls durch Halogen substituiertes Benzyl oder -(CH₂)_n-Z ist, worin n 1 oder 2 ist und Z die gleichen Bedeutungen hat, wie sie unten angegeben sind, und

R⁵ und R⁶ Wasserstoff, C₁₋₉-Alkyl, das gegebenenfalls durch wenigstens einen Substituenten, ausgewählt aus der aus Halogen, Hydroxy, Mercapto, C₁₋₂-Alkoxy, C₁₋₂-Alkylthio, C₃₋₆-Cycloalkyl, Amino, C₁₋₂-Monoalkylamino, C₂₋₄(insgesamt)-Dialkylamino, Carboxy, C₁₋₂-Alkoxy-carbonyl und Cyan bestehenden Gruppe, substituiert ist, C₃₋₄-Alkenyl, das gegebenenfalls durch Halogen substituiert ist, C₃₋₄-Alkynyl, gegebenenfalls durch Chlor substituiertes Phenyl, gegebenenfalls durch Chlor substituiertes Benzyl, C₁₋₄-Alkoxy, Hydroxy, Formyl, C₁₋₄-Alkoxy-carbonyl, C₁₋₄-Alkylamino, C₂₋₄-(insgesamt)-Dialkylamino, Amino, Acyl oder

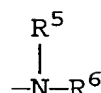


sind, worin
 R¹ und m die oben angegebenen Bedeutungen haben und Z die gleichen Bedeutungen hat, wie sie unten angegeben sind, und außerdem
 R⁵ und R⁶ zusammen mit dem N-Atom, an das sie gebunden sind, einen 3- bis 7-gliedrigen Ring bilden können, der durch C₁₋₂-Alkyl substituiert sein kann und N, O oder S als Glied des Ringes neben dem N-Atom, an das sie gebunden sind, enthalten kann, und
 Z eine 5-gliedrige heterocyclische Gruppe, die durch Halogen oder C₁₋₂-Alkyl substituiert ist und ein oder zwei Stickstoff-Atome oder ein Stickstoff-Atom und entweder ein Sauerstoff-Atom oder ein Schwefel-Atom enthält, oder
 eine 6-gliedrige heterocyclische Gruppe, die durch Halogen oder C₁₋₂-Alkyl substituiert ist und ein oder zwei Stickstoff-Atome ist, mit der Maßgabe ist, daß,

wenn
 Z durch Halogen substituiertes Pyridyl ist,
 m 1 ist,
 R² C₁₋₆-Alkyl ist und
 R³ -S-Alkyl(C₁₋₆) oder -S-Benzyl ist,
 dann
 R¹ Cyan oder C₁₋₄-Alkyl ist, und
 weiterhin mit Ausnahme von
 N-Cyan-N'-methyl-N''-[(4-methylthiazol-2-yl)methyl]guanidin.

8. Verbindungen der Formel (I) nach Anspruch 7, worin

R¹ Wasserstoff, Methyl, Ethyl oder Propyl ist,
 m 1 ist,
 R² Wasserstoff, Methyl, Ethyl, Propyl, Allyl, Propargyl, gegebenenfalls durch Chlor substituiertes Phenyl, Hydroxy, Methoxy, Ethoxy oder Pyridylmethyl ist, das gegebenenfalls durch Chlor substituiert ist,
 R³ -O-R⁴, -S-R⁴, oder



5

ist, worin

R^4 C_{1-3} -Alkyl, Allyl, Propargyl, Cyclohexyl, Phenyl, gegebenenfalls durch Chlor substituiertes Benzyl oder gegebenenfalls durch Chlor substituiertes Pyridylmethyl ist,

10

R^5 und R^6 Wasserstoff, C_{1-4} -Alkyl, das gegebenenfalls durch Fluor oder Chlor substituiert ist, Allyl, das gegebenenfalls durch Chlor substituiert ist, Propargyl, gegebenenfalls durch Chlor substituiertes Phenyl, gegebenenfalls durch Chlor substituiertes Benzyl, Methoxy, Hydroxy, Hydroxyethyl, C_{1-2} -Alkylamino, Dimethylamino, Amino, Cyanethyl, 2-Chlor-5-pyridylmethyl oder 2-Chlor-5-thiazolylmethyl sind, und außerdem

15

R^5 und R^6 zusammen mit dem N-Atom, an das sie gebunden sind, Pyrrolidino, Piperidino, 2-Methyl-piperidino, Morpholino, Piperazino oder Isoxazolidino bilden können, und

Z eine 5-gliedrige heterocyclische Gruppe, die durch Halogen oder C_{1-2} -Alkyl substituiert ist und ein oder zwei Stickstoff-Atome oder ein Stickstoff-Atom und entweder ein Sauerstoff-Atom oder ein Schwefel-Atom enthält, oder

20

eine 6-gliedrige heterocyclische Gruppe, die durch Halogen oder C_{1-2} -Alkyl substituiert ist und ein oder zwei Stickstoff-Atome ist, mit der Maßgabe ist, daß,

wenn

Z durch Halogen substituiertes Pyridyl ist,

m 1 ist,

R^2 Methyl, Ethyl oder Propyl ist und

25

R^3 -S-Alkyl(C_{1-3}) oder -S-Benzyl ist,

dann

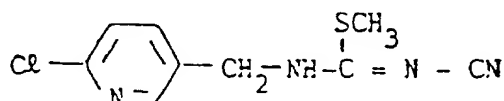
R^1 Methyl, Ethyl oder Propyl ist, und

weiterhin mit Ausnahme von N-Cyan-N'-methyl-N''-[(4-methylthiazol-2-yl)methyl]guanidin.

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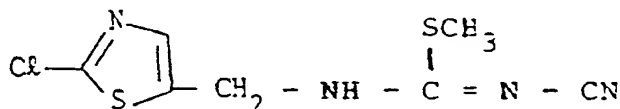
9. Verbindungen nach Anspruch 7, worin eine solche Verbindung S-Methyl-N (2-chlor-5-pyridylmethyl)-N'-cyanisothioharnstoff der nachstehenden Formel

35



S-Methyl-N-(2-chloro-5-thiazolylmethyl)-N'-cyanisothioharnstoff der nachstehenden Formel

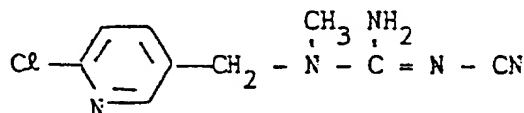
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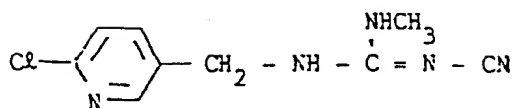
3-(2-Chlor-5-pyridylmethyl)-3-methyl-2-cyanguanidin der nachstehenden Formel

50

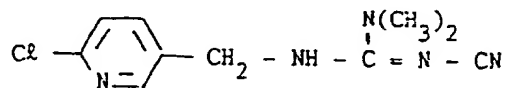


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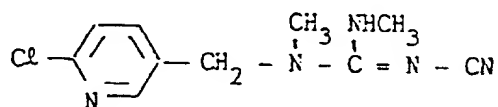
3-(2-Chlor-5-pyridylmethyl)-1-methyl-2-cyanguanidin der nachstehenden Formel



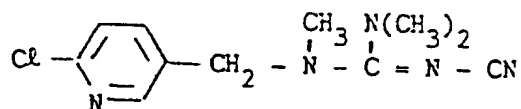
3-(2-Chlor-5-pyridylmethyl)-1,1-dimethyl-2-cyanguanidin der nachstehenden Formel



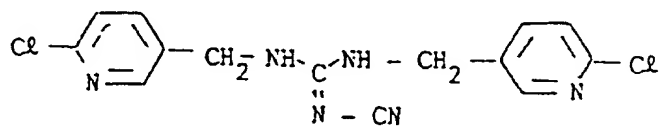
3-(2-Chlor-5-pyridylmethyl)-1,3-dimethyl-2-cyanguanidin der nachstehenden Formel



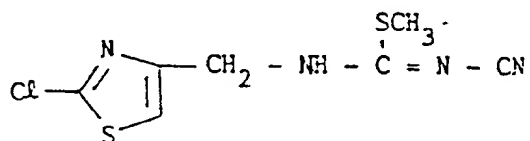
3-(2-Chlor-5-pyridylmethyl)-1,1,3-trimethyl-2-cyanguanidin der nachstehenden Formel



1,3-Bis-(2-Chlor-5-pyridylmethyl)-2-cyanguanidin der nachstehenden Formel

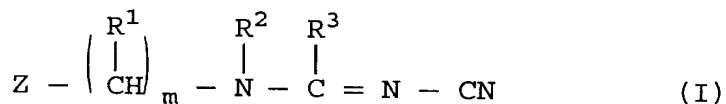


und
S-Methyl-N-(2-chloro-5-thiazolylmethyl)-N'-cyanisothioharnstoff der nachstehenden Formel



ist.

10. Verfahren zur Herstellung von Cyan-Verbindungen der Formel (I) nach Anspruch 7

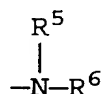


worin

R¹ Wasserstoff, Cyan oder C₁₋₄-Alkyl ist,
m 1 ist,

R² Wasserstoff, C₁₋₆-Alkyl, C₃₋₄-Alkenyl, das gegebenenfalls durch Halogen substituiert
ist, C₃₋₄-Alkynyl, C₃₋₈-Cycloalkyl, das gegebenenfalls durch Methyl substituiert ist,
gegebenenfalls durch Halogen substituiertes Phenyl, gegebenenfalls durch Halogen
substituiertes Benzyl, Hydroxy, C₁₋₄-Alkoxy oder -CH₂-Z ist, worin Z die gleichen
Bedeutungen hat, wie sie unten angegeben sind,

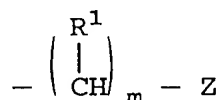
R³ -O-R⁴, -S-R⁴, oder



ist, worin

R⁴ C₁₋₆-Alkyl, C₃₋₄-Alkenyl, C₃₋₄-Alkynyl, C₃₋₈-Cycloalkyl, gegebenenfalls durch Halo-
gen substituiertes Phenyl, gegebenenfalls durch Halogen substituiertes Benzyl oder
-(CH₂)_n-Z ist, worin n 1 oder 2 ist und Z die gleichen Bedeutungen hat, wie sie unten
angegeben sind, und

R⁵ und R⁶ Wasserstoff, C₁₋₉-Alkyl, das gegebenenfalls durch wenigstens einen Substituenten,
ausgewählt aus der aus Halogen, Hydroxy, Mercapto, C₁₋₂-Alkoxy, C₁₋₂-Alkylthio,
C₃₋₆-Cycloalkyl, Amino, C₁₋₂-Monoalkylamino, C₂₋₄ (insgesamt)-Dialkylamino, Car-
boxy C₁₋₂-Alkoxy-carbonyl und Cyan bestehenden Gruppe, substituiert ist C₃₋₄-
Alkenyl, das gegebenenfalls durch Halogen substituiert ist, C₃₋₄-Alkynyl, gegeben-
enfalls durch Chlor substituiertes Phenyl, gegebenenfalls durch Chlor substituiertes
Benzyl, C₁₋₄-Alkoxy, Hydroxy, Formyl, C₁₋₄-Alkoxy-carbonyl, C₁₋₄-Alkylamino, C₂₋₄-
(insgesamt)-Dialkylamino, Amino, Acyl oder



sind, worin

R¹ und m die oben angegebenen Bedeutungen haben und Z die gleichen Bedeutungen
hat, wie sie unten angegeben sind, und außerdem

R⁵ und R⁶ zusammen mit dem N-Atom, an das sie gebunden sind, einen 3- bis 7-gliedrigen Ring
bilden können, der durch C₁₋₂-Alkyl substituiert sein kann und N, O oder S als Glied
des Ringes neben dem N-Atom, an das sie gebunden sind, enthalten kann, und

Z eine 5-gliedrige heterocyclische Gruppe, die durch Halogen oder C₁₋₂-Alkyl substitu-
iert ist und ein oder zwei Stickstoff-Atome oder ein Stickstoff-Atom und entweder ein
Sauerstoff-Atom oder ein Schwefel-Atom enthält, oder eine 6-gliedrige heterocycli-
sche Gruppe, die durch Halogen oder C₁₋₂-Alkyl substituiert ist und ein oder zwei
Stickstoff-Atome ist, mit der Maßgabe ist, daß,

wenn

Z durch Halogen substituiertes Pyridyl ist,
m 1 ist,

R² C₁₋₆-Alkyl ist und

R³ -S-Alkyl(C₁₋₆) oder -S-Benzyl ist,

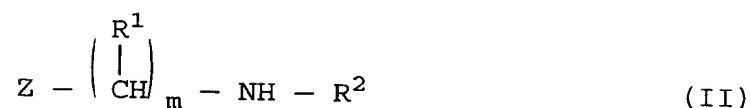
dann

R¹ Cyan oder C₁₋₄-Alkyl ist, und

weiterhin mit Ausnahme von

N-Cyan-N'-methyl-N''-[(4-methylthiazol-2-yl)methyl]guanidin,
dadurch gekennzeichnet, daß

a) in dem Fall, in dem R³ -S-R⁴ ist,
Verbindungen der Formel (II)



worin

R^1 , m , R^2 und Z die oben angegebenen Bedeutungen haben,
mit Verbindungen der Formel (III)



worin

R^4 die oben angegebenen Bedeutungen hat,
in Gegenwart inerter Lösungsmittel umgesetzt werden,

oder

b) in dem Fall, in dem $R^3 - O - R^4$ ist,
die obengenannten Verbindungen der Formel (II)
mit Verbindungen der Formel (IV)

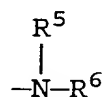


worin

R^4 die oben angegebenen Bedeutungen hat,
in Gegenwart inerter Lösungsmittel umgesetzt werden,

oder

c) in dem Fall, in dem R^3



ist,

die obengenannten Verbindungen der Formel (II)
mit Verbindungen der Formel (V)



worin

R^4 , R^5 und R^6 die oben angegebenen Bedeutungen haben,
in Gegenwart inerter Lösungsmittel umgesetzt werden,

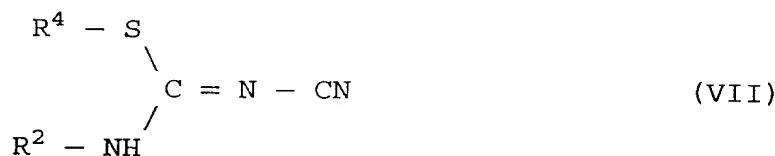
oder

d) in dem Fall, in dem R^3 -S- R^4 ist und m 1 ist,
Verbindungen der Formel (VI)



worin

R^1 und Z die oben angegebenen Bedeutungen haben und M Halogen ist,
mit Verbindungen der Formel (VII)



worin

R^2 und R^4 die oben angegebenen Bedeutungen haben,
in Gegenwart inerter Lösungsmittel und gegebenenfalls in Gegenwart einer Base umgesetzt werden.

Revendications

1. Utilisation de composés cyano de la formule (I)



dans laquelle

- R^1 représente un atome d'hydrogène, un radical cyano ou alkyle en C_{1-4} ,
- m représente 0 ou 1,
- R^2 représente un atome d'hydrogène, un radical alkyle en C_{1-6} alkényle en C_{3-4} facultativement halogéno-substitué, alkynyle en C_{3-4} , cycloalkyle en C_{3-8} facultativement substitué par un radical méthyle, phényl facultativement halogéno-substitué, benzyle facultativement halogéno-substitué, hydroxy, alcoxy en C_{1-4} ou -CH₂-Z dans lequel Z a la même signification que ci-dessous,
- R^3 représente -O- R^4 , -S- R^4 ou



dans lesquels

R^4 représente un radical alkyle en C_{1-6} , alkényle en C_{3-4} , alkynyle en C_{3-4} , cycloalkyle en C_{3-8} , phényle facultativement halogéno-substitué, benzyle facultativement halogéno-substitué ou -(CH₂)_n-Z dans lequel n représente 1 ou 2 et Z a la même signification que ci-dessous, et R^5 et R^6 représentent un atome d'hydrogène, un radical alkyle en C_{1-9} facultativement substitué par au moins un radical choisi dans le groupe constitué des radicaux halogène, hydroxy, mercapto, alcoxy en C_{1-2} , alkylthio en C_{1-2} , cycloalkyle en C_{3-6} , amino, monoalkylamino en C_{1-2} , dialkylamino en C_{2-4} (en tout), carboxy, (alcoxy en C_{1-2}) carbonyle et cyano, alkényle en C_{3-4} facultativement halogéno-substitué, alkynyle en C_{3-4} , phényle facultativement chloro-substitué, benzyle facultativement chloro-substitué, alcoxy en C_{1-4} , hydroxy, formyle, (alcoxy en C_{1-4})

carbonyle, alkylamino en C₁₋₄, dialkylamino en C₂₋₄ (en tout), amino, acyle ou -(CH-R¹)_m-Z, dans lequel R¹ et m ont la même signification que ci-dessus, et Z a la même signification que ci-dessous, et en outre

R⁵ et R⁶ peuvent former, ensemble avec l'atome de N auquel ils sont liés, un cycle de 3 à 7 membres qui peut être substitué par un radical alkyle en C₁₋₂ et peut contenir N, O ou S comme membre dudit cycle, en plus de l'atome N auquel ils sont liés, et

Z représente un hétérocycle à 5 membres qui est substitué par un halogène ou un radical alkyle en C₁₋₂ et contient un à deux atomes d'azote, ou un atome d'azote et soit un atome d'oxygène soit un atome de soufre, ou un hétérocycle à 6 membres qui est substitué par un halogène ou un radical alkyle en C₁₋₂ et contient un ou deux atomes d'azote,

à la condition que quand Z représente un radical pyridyle halogéno-substitué, m représente 1, R² représente un radical alkyle en C₁₋₆ et R³ représente un radical -S-alkyl(C₁₋₆) ou -S-benzyle, alors R¹ représente un radical cyano ou alkyle en C₁₋₄

pour combattre les insectes nuisibles.

2. Utilisation des composés de la formule (I) selon la revendication 1 où

- R¹ représente un atome d'hydrogène, ou un radical alkyle en C₁₋₃,
- m représente 0 ou 1,
- R² représente un atome d'hydrogène, un radical alkyle en C₁₋₄, allyle, propargyle, phényle facultativement halogéno-substitué, benzyle facultativement halogéno-substitué, hydroxy, alcoxy en C₁₋₃ ou -CH₂-Z¹ dans lequel Z¹ représente un radical pyridyle halogéno-substitué,
- R³ représente -O-R⁴, -S-R⁴ ou



dans lesquels

R⁴ représente un radical alkyle en C₁₋₄, allyle, propargyle, cycloalkyle en C₃₋₆, phényle facultativement halogéno substitué, benzyle facultativement halogéno-substitué ou -CH₂-Z¹ où Z¹ a la même signification que ci-dessus, et

R⁵ et R⁶ représentent un atome d'hydrogène, un radical alkyle en C₁₋₉ facultativement fluoro- ou chloro-substitué, allyle facultativement chloro-substitué, propargyle, phényle facultativement chloro-substitué, benzyle facultativement chloro-substitué, alcoxy en C₁₋₃, hydroxy, hydroxy-C₁₋₂ alkyle, mercapto-C₁₋₂ alkyle, amino-C₁₋₂ alkyle, alkylamino en C₁₋₃, diméthylamino, amino, cyano-C₁₋₂ alkyle, pyridyle facultativement substitué par un chlore ou un radical méthyle ou -CH₂-Z², dans lequel Z² représente un radical pyridyle facultativement substitué par halogène ou 5-thiazolyle facultativement halogéno-substitué, et en outre R⁵ et R⁶ peuvent former, ensemble avec l'atome de N auquel ils sont liés, un cycle de 3 à 6 membres qui peut être substitué par un radical méthyle et peut contenir N, O ou S comme membre dudit cycle, en plus de l'atome N auquel ils sont liés, et

Z représente un hétérocycle à 5 membres qui est substitué par un halogène ou un radical alkyle en C₁₋₂ et contient un ou deux atomes d'azote, ou un atome d'azote et soit un atome d'oxygène soit un atome de soufre, ou un hétérocycle à 6 membres qui est substitué par un halogène ou un radical alkyle en C₁₋₂ et contient un ou deux atomes d'azote,

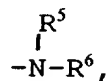
à la condition que quand Z représente un radical pyridyle halogéno-substitué, m représente 1, R² représente un radical alkyle en C₁₋₄ et R³ représente un radical -S-alkyl(C₁₋₄) ou -S-benzyle, alors R¹ représente un radical alkyle en C₁₋₃

pour combattre les insectes nuisibles.

3. Utilisation selon la revendication 1 des composés de la formule (I) dans laquelle

- R¹ représente un atome d'hydrogène, un radical méthyle, éthyle ou propyle,
- m représente 0 ou 1,
- R² représente un atome d'hydrogène, un radical méthyle, éthyle, propyle, allyle, propargyle, phényle facultativement chloro-substitué, hydroxy, méthoxy, éthoxy ou pyridylméthyle facultativement chloro-substitué,

- R³ représente -O-R⁴, -S-R⁴ ou



dans lesquels

R⁴ représente un radical alkyle en C₁₋₃, allyle, propargyle, cyclohexyle, phényle, benzyle facultativement chloro-substitué, pyridylméthyle facultativement chloro-substitué,

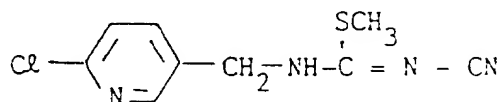
R⁵ et R⁶ représentent un atome d'hydrogène, un radical alkyle en C₁₋₄ facultativement fluoro- ou chloro-substitué, allyle facultativement chloro-substitué, propargyle, phényle facultativement chloro-substitué, benzyle facultativement chloro-substitué, méthoxy, hydroxy, hydroxyéthyle, alkylamino en C₁₋₂, diméthylamino, amino, cyanoéthyle, 2-chloro-5-pyridylméthyle ou 2-chloro-5-thiazolylméthyle, et en outre,

R⁵ et R⁶ peuvent former, ensemble avec l'atome d'azote auquel ils sont liés, un radical pyrrolidino, pipéridino, 2-méthylpipéridino, morpholino, pipérazino ou isoxazolidino, et

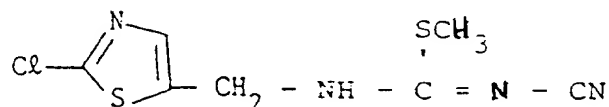
Z représente un hétérocycle à 5 membres qui est substitué par un halogène ou un radical alkyle en C₁₋₂ et contient un ou deux atomes d'azote, ou un atome d'azote et soit un atome d'oxygène soit un atome de soufre, ou un hétérocycle à 6 membres qui est substitué par un halogène ou un radical alkyle en C₁₋₂ et contient un ou deux atomes d'azote,

à la condition que quand Z représente un radical pyridyle halogéno-substitué, m représente 1, R² représente un radical méthyle, éthyle ou propyle et R³ représente -S-alkyl(C₁₋₃) ou -S-benzyle, alors R¹ représente un radical méthyle, éthyle ou propyle, pour combattre les insectes nuisibles.

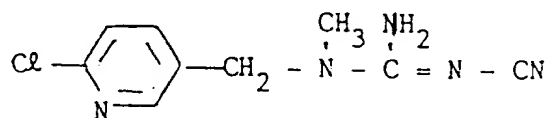
4. Utilisation selon la revendication 1 de composés qui sont la S-méthyl-N-(2-chloro-5-pyridylméthyl)-N'-cyanoisothiourée de la formule suivante



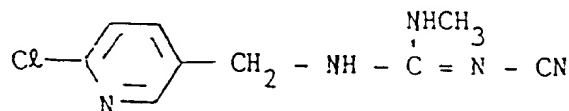
la S-méthyl-N-(2-chloro-5-thiazolylméthyl)-N'-cyanoisothiourée de la formule suivante



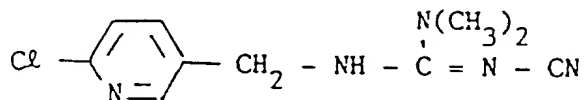
la 3-(2-chlor-5-pyridylméthyl)-3-méthyl-2-cyanoguanidine de la formule suivante



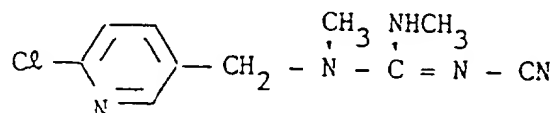
la 3-(2-chlor-5-pyridylméthyl)-1-méthyl-2-cyanoguanidine de la formule suivante



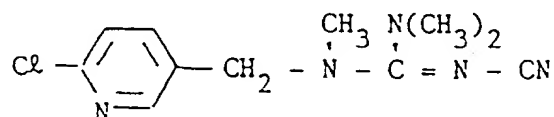
la 3-(2-chloro-5-pyridylméthyl)-1,1-diméthyl-2-cyanoguanidine de la formule suivante



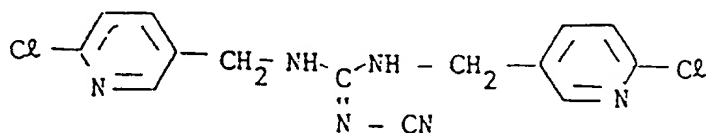
la 3-(2-chloro-5-pyridylméthyl)-1,3-diméthyl-2-cyanoguanidine de la formule suivante



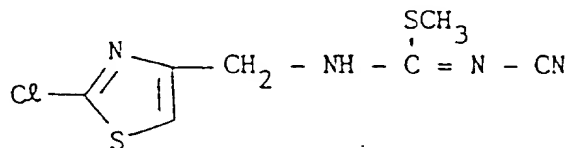
la 3-(2-chloro-5-pyridylméthyl)-1,1,3-triméthyl-2-cyanoguanidine de la formule suivante



la 1,3-bis(chloro-5-pyridylméthyl)-2-cyanoguanidine de la formule suivante



et la S-méthyl-N-(2-chloro-5-thiazolylméthyl)-N'-cyanoisothiourée de la formule suivante



pour combattre les insectes nuisibles.

5. Compositions insecticides, caractérisées en ce qu'elles contiennent au moins un composé cyano de la formule (I) selon la revendication 1.

6. Procédé de préparation des compositions insecticides, caractérisé en ce que les composés cyano de la formule (I) selon la revendication 1 sont mélangés avec des diluants et/ou des agents tensio-actifs.

7. Composés cyano de la formule (I)



dans laquelle

- R¹ représente un atome d'hydrogène, un radical cyano ou alkyle en C₁₋₄,

- m représente 1,
- R² représente un atome d'hydrogène, un radical alkyle en C₁₋₆, alkényle en C₃₋₄ facultativement halogéno-substitué, alkynyle en C₃₋₄, cycloalkyle en C₃₋₈ facultativement substitué par un radical méthyle, phényle facultativement halogéno-substitué, benzyle facultativement halogéno-substitué, hydroxy, alcoxy en C₁₋₄ ou -CH₂-Z dans lequel Z a la même signification que ci-dessous,
- R³ représente -O-R⁴, -S-R⁴ ou



dans lesquels

R⁴ est un radical alkyle en C₁₋₆, alkényle en C₃₋₄, alkynyle en C₃₋₄, cycloalkyle en C₃₋₈, phényle facultativement halogéno-substitué, benzyle facultativement halogéno-substitué ou -(CH₂)_n-Z dans lequel n représente 1 ou 2 et Z a la même signification que ci-dessous, et

R⁵ et R⁶ représente un atome d'hydrogène, un radical alkyle en C₁₋₉ facultativement substitué par au moins un radical choisi dans le groupe constitué des radicaux halogène, hydroxy, mercapto, alcoxy en C₁₋₂, alkylthio en C₁₋₂, cycloalkyle en C₃₋₆, amino, monoalkylamino en C₁₋₂, dialkylamino en C₂₋₄ (en tout), carboxy, (alcoxy en C₁₋₂) carbonyle et cyano, alkényle en C₃₋₄ facultativement halogéno-substitué, alkynyle en C₃₋₄, phényle facultativement chloro-substitué, benzyle facultativement chloro-substitué, alcoxy en C₁₋₄, hydroxy, formyle, (alcoxy en C₁₋₄)-carbonyle, alkylamino en C₁₋₄, dialkylamino en C₂₋₄ (en tout), amino, acyle ou -(CH-R¹)_m-Z, dans lequel R¹ et m ont la même signification que ci-dessus, et Z a la même signification que ci-dessous, et en outre

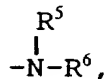
R⁵ et R⁶ peuvent former, ensemble avec l'atome de N auquel ils sont liés, un cycle de 3 à 7 membres qui peut être substitué par un radical alkyle en C₁₋₂ et peut contenir N, O ou S comme membre dudit cycle, en plus de l'atome N auquel ils sont liés, et

Z représente un hétérocycle à 5 membres qui est substitué par un halogène ou un radical alkyle en C₁₋₂ et contient un à deux atomes d'azote, ou un atome d'azote et soit un atome d'oxygène soit un atome de soufre, ou un hétérocycle à 6 membres qui est substitué par un halogène ou un radical alkyle en C₁₋₂ et contient un ou deux atomes d'azote,

à la condition que quand Z représente un radical pyridyle halogéno-substitué, m représente 1, R² représente un radical alkyle en C₁₋₆ et R³ représente un radical -S-alkyl(C₁₋₆) ou -S-benzyle, alors R¹ représente un radical cyano ou alkyle en C₁₋₄ à l'exception de la N-cyano-N'-méthyl-N''-[4-méthylthiazol-2-yl)méthyl]guanidine.

8. Composés de la formule (I) selon la revendication 7 dans laquelle

- R¹ représente un atome d'hydrogène, un radical méthyle, éthyle ou propyle,
- m représente 1,
- R² représente un atome d'hydrogène, un radical méthyle, éthyle, propyle, allyle, propargyle, phényle facultativement chloro-substitué, hydroxy, méthoxy, éthoxy ou pyridylméthyle facultativement chloro-substitué,
- R³ représente -O-R⁴, -S-R⁴ ou



dans lesquels

R⁴ représente un radical alkyle en C₁₋₃, allyle, propargyle, cyclohexyle, phényle, benzyle facultativement chloro-substitué, pyridylméthyle facultativement chloro-substitué,

R⁵ et R⁶ représentent un atome d'hydrogène, un radical alkyle en C₁₋₄ facultativement fluoro- ou chloro-substitué, allyle facultativement chloro-substitué, propargyle, phényle facultativement chloro-substitué, benzyle facultativement chloro-substitué, méthoxy, hydroxy, hydroxyéthyle, alkylamino en C₁₋₂, diméthylamino, amino, cyanoéthyle, 2-chloro-5-pyridylméthyle ou 2-chloro-5-thiazo-

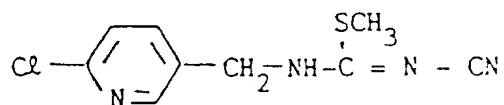
ylméthyle, et en outre,

R⁵ et R⁶ peuvent former, ensemble avec l'atome d'azote auquel ils sont liés, un radical pyrrolidino, pipéridino, 2-méthylpipéridino, morpholino, pipérazino ou isoxazolidino, et

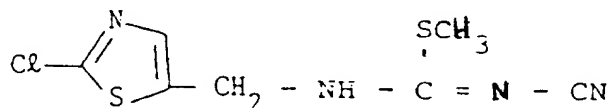
Z représente un hétérocycle à 5 membres qui est substitué par un halogène ou un alkyle en C₁₋₂ et contient un ou deux atomes d'azote, ou un atome d'azote et soit un atome d'oxygène soit un atome de soufre, ou un hétérocycle à 6 membres qui est substitué par un halogène ou un radical alkyle en C₁₋₂ et contient un ou deux atomes d'azote,

à la condition que quand Z représente un radical pyridyle halogéno-substitué, m représente 1, R² représente un radical méthyle, éthyle ou propyle et R³ représente un radical -S-alkyl(C₁₋₃) ou -S-benzyle, alors R¹ représente un radical méthyle, éthyle ou propyle, et de plus à l'exception de la N-cyano-N'-méthyl-N''-[(4-méthylthiazol-2-yl)méthyl]guanidine.

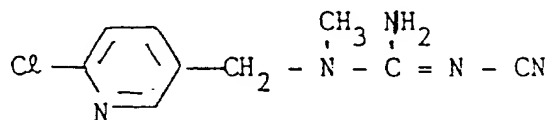
9. Composés selon la revendication 7, qui sont la S-méthyl-N-(2-chloro-5-pyridylméthyl)-N'-cyanisothiourée de la formule suivante



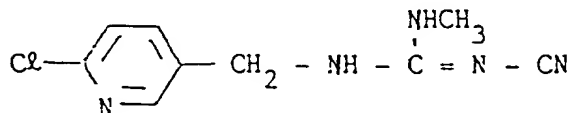
la S-méthyl-N-(2-chloro-5-thiazolylméthyl)-N'-cyanisothiourée de la formule suivante



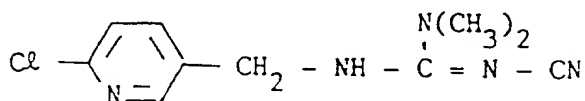
la 3-(2-chloro-5-pyridylméthyl)-3-méthyl-2-cyanoguanidine de la formule suivante



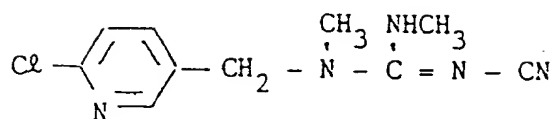
la 3-(2-chloro-5-pyridylméthyl)-1-méthyl-2-cyanoguanidine de la formule suivante



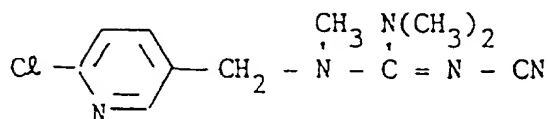
la 3-(2-chloro-5-pyridylméthyl)-1,1-diméthyl-2-cyanoguanidine de la formule suivante



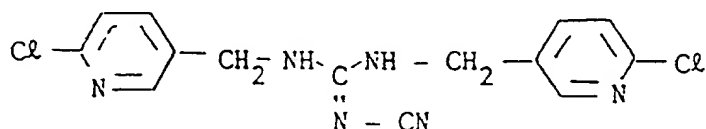
la 3-(2-chloro-5-pyridylméthyl)-1,3-diméthyl-2-cyanoguanidine de la formule suivante



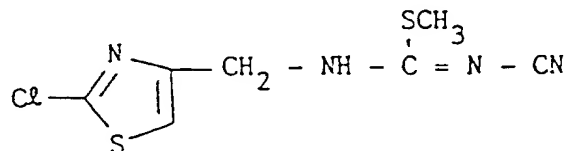
la 3-(2-chloro-5-pyridylméthyl)-1,1,3-triméthyl-2-cyanoguanidine de la formule suivante



la 1,3-bis(chloro-5-pyridylméthyl)-2-cyanoguanidine de la formule suivante



et la S-méthyl-N-(2-chloro-5-thiazolylméthyl)-N'-cyanisothiourée de la formule suivante



10. Procédé de préparation des composés cyano de la formule (I) selon la revendication 7



dans laquelle

- R¹ représente un atome d'hydrogène, un radical cyano ou alkyle en C₁₋₄,
- m représente 1,
- R² représente un atome d'hydrogène, un radical alkyle en C₁₋₆, alkényle en C₃₋₄ facultativement halogéno-substitué, alkynyle en C₃₋₄, cycloalkyle en C₃₋₈ facultativement substitué par un radical méthyle, phényle facultativement halogéno-substitué, benzyle facultativement halogéno-substitué, hydroxy, alcoxy en C₁₋₄ ou -CH₂-Z dans lequel Z a la même signification que ci-dessous,
- R³ représente -O-R⁴, -S-R⁴ ou



dans lesquels

R⁴ représente un radical alkyle en C₁₋₆, alkényle en C₃₋₄, alkynyle en C₃₋₄, cycloalkyle en C₃₋₈, phényle facultativement halogéno-substitué, benzyle facultativement halogéno-substitué ou -(CH₂)_n-Z dans lequel n représente 1 ou 2 et Z a la même signification que ci-dessous, et

R⁵ et R⁶ sont hydrogène, radical alkyle en C₁₋₉ facultativement substitué par au moins un radical choisi dans le groupe constitué des radicaux halogène, hydroxy, mercapto, alcoxy en C₁₋₂, alkylthio en C₁₋₂, cycloalkyle en C₃₋₆ amino, monoalkylamino en C₁₋₂, dialkylamino en C₂₋₄ (en tout), carboxy, (alcoxy en C₁₋₂)carbonyle et cyano, alkényle en C₃₋₄ facultativement halogéno-substitué, alkynyle en C₃₋₄, phényle facultativement chloro-substitué, benzyle facultativement chloro-substitué, alcoxy en C₁₋₄, hydroxy, formyle, (alcoxy en C₁₋₄)carbonyle, alkylamino en C₁₋₄, dialkylamino en C₂₋₄ (en tout), amino, acyle ou -(CH-R¹)_m-Z, dans lequel R¹ et m ont la même signification que ci-dessus, et Z a la même signification que ci-dessus, et en addition

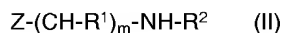
R⁵ et R⁶ peuvent former, ensemble avec l'atome de N auquel ils sont liés, un cycle de 3 à 7 membres qui peut être substitué par un radical alkyle en C₁₋₂ et peut contenir N, O ou S comme membre dudit cycle, en plus de l'atome N auquel ils sont liés, et

à la condition que quand Z représente un radical pyridyle halogéno-substitué, m représente 1, R² représente un radical alkyle en C₁₋₆ et R³ représente un radical -S-alkyl(C₁₋₆) ou -S-benzyle, alors R¹ représente un radical cyano ou alkyle en C₁₋₄ à l'exception de la N-cyano-N'-méthyl-N"-[(4-méthylthiazol-2-yl)méthyl]guanidine,

caractérisé en ce que

a) dans le cas où R³ représente -S-R⁴;

les composés de la formule (II)



dans laquelle R¹, m, R² et Z ont la même signification que ci-dessus,

sont mis à réagir avec des composés de la formule (III)



dans laquelle R⁴ a la même signification que ci-dessus,

en présence de solvants inertes,

ou

b) dans le cas où R³ représente -O-R⁴;

les composés ci-avant cités de la formule (II) sont mis à réagir avec des composés de la formule (IV)

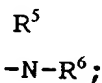


dans laquelle R⁴ a la même signification que ci-dessus,

en présence de solvants inertes,

ou

c) dans le cas où R³ représente

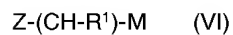


les composés ci-avant cités de la formule (II) sont mis à réagir avec des composés de la formule (V)

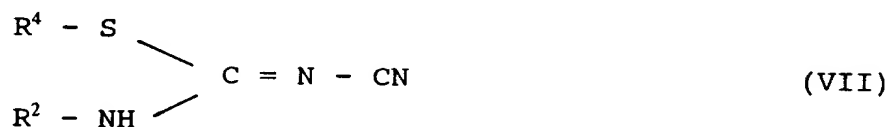


dans laquelle R^4 , R^5 et R^6 ont les mêmes significations que ci-dessus,
en présence de solvants inertes,
ou

d) dans le cas où R^3 représente $-\text{S}-\text{R}^4$ et m représente 1; les composés de la formule (VI)



dans laquelle R^1 et Z ont les mêmes significations que ci-dessus et M représente un halogène,
sont mis à réagir avec des composés de la formule (VII)



dans laquelle R^2 et R^4 ont les mêmes significations que ci-dessus,
en présence de solvants inertes et, si approprié, en présence d'une base.